

FORM PTO-1390
(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

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OHS-304

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (if known, see 37 CFR 1.5

09/890326

INTERNATIONAL APPLICATION NO.

PCT/JP00/00515

INTERNATIONAL FILING DATE

01 January 2000

PRIORITY DATE CLAIMED

01 February 1999

TITLE OF INVENTION

SURFACE-PROTECTED TRANSPARENT PLASTIC COMPOSITE MATERIAL

APPLICANT(S) FOR DO/EO/US

Tatsuya EKINAKA, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☒ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information: Copy of PCT/IB/308

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OHS-304

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

Tatsuya EKINAKA, et al.

Serial No.: Unassigned

Group:

Filed: Concurrently

Examiner:

FOR: SURFACE-PROTECTED TRANSPARENT PLASTIC COMPOSITE MATERIAL

Date: July 30, 2001

The Hon. Commissioner of
Patents and Trademarks
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir:

Preliminary to examination, please amend the herewith filed application as follows:

IN THE CLAIMS

Please amend the claims as follows:

Please amend claims 4 and 6 as follows, a marked-up copy of these claims showing the amendments made is attached:

4. (Amended) The transparent plastic composite material of claim 1, wherein the coating layer (I) is formed of a mixture of the acrylic resin with a hydrolysis condensate of a compound of the following formula (I-e),

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[illegible]

6. (Amended) The transparent plastic composite material of claim 1, wherein the coating layer (I) further contains 0.7 to 100 parts by weight, per 100 parts by weight of the acrylic resin, of an ultraviolet absorbent.

--19 (New) The transparent plastic composite material of claim 2, wherein the coating layer (I) is formed of a mixture of the acrylic resin with a hydrolysis condensate of a compound of the following formula (I-e),

Wherein R⁷ is an alkyl group having 1 to 4 carbon atoms, a vinyl group or an alkyl group which is substituted with one or more groups selected from the class consisting of methacryloxy, amino, glycidoxy and 3,4-epoxycyclohexyl and has 1 to 3 carbon atoms, R⁸ is an alkyl group having 1 to 4 carbon atoms, and r is an integer of 0 to 2, the mixture having an acrylic

an integer of 0 to 2, the mixture having an acrylic resin:hydrolysis condensate (as $R^7_r-SiO_{4-r/2}$) amount ratio by weight in the range of from 99:1 to 60:40.

24. (New) The transparent plastic composite material of claim 23, wherein the coating layer (I) further contains a melamine resin in the range of from 1 to 20 parts by weight per 100 parts by weight of the total of the acrylic resin and the hydrolysis condensate of the compound of the formula (I-e).

25. (New) The transparent plastic composite material of claim 24, wherein the coating layer (I) further contains 0.7 to 100 parts by weight, per 100 parts by weight of the acrylic resin, of an ultraviolet absorbent.

26. (New) The transparent plastic composite material of claim 25, wherein the ultraviolet absorbent has a solubility of 1.5g/L or less in a solvent mixture containing 100 parts by weight of isopropanol, 30 parts by weight of methanol and 15 parts by weight of water when measured at 25°C.--

REMARKS

Entry of the foregoing amendments prior to examination of this application is respectfully requested in view of the following comments.

Claims 4 and 6 have been amended to eliminate improper multiple dependency and new claims 19-26 have been added presenting the previous multiple dependent claims in proper

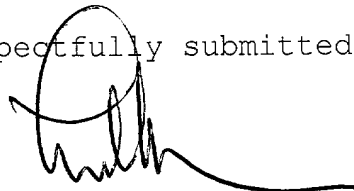
single dependent form. Accordingly, claims 1-26 are pending in this application.

The amendment of claims 4 and 6 eliminates all multiple dependent claims and corrects the improper multiple dependency that was present in claims 6 and 7. With this amendment, claims 4-7 now present a set of claims in proper single dependent form that are dependent from claim 1.

New claims 19-26 correspond to claims 4-7 rewritten in proper single dependent form as two sets of identical claims with one set, claims 19-22, dependent from claim 2 and the other set, claims 23-26, dependent from claim 3.

No new matter has been added and applicants respectfully submit that this application is in condition for allowance and an early notice to that effect is earnestly solicited.

Respectfully submitted,



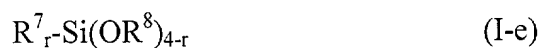
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Serial No.: Unassigned
Filed: July 30, 2001
Docket No.: OHS-304

MARKED-UP COPY OF AMENDED CLAIMS

4. (Amended) The transparent plastic composite material of [any one of claims] claim 1 [to 3], wherein the coating layer (I) is formed of a mixture of the acrylic resin with a hydrolysis condensate of a compound of the following formula (I-e),



Wherein R^7 is an alkyl group having 1 to 4 carbon atoms, a vinyl group or an alkyl group which is substituted with one or more groups selected from the class consisting of methacryloxy, amino, glycidoxy and 3,4-epoxycyclohexyl and has 1 to 3 carbon atoms, R^8 is an alkyl group having 1 to 4 carbon atoms, and r is an integer of 0 to 2, the mixture having an acrylic resin:hydrolysis condensate (as $R^7_r-SiO_{4-r/2}$) amount ratio by weight in the range of from 99:1 to 60:40.

6. (Amended) The transparent plastic composite material of [any one of claims] claim 1 [to 4], wherein the coating layer (I) further contains 0.7 to 100 parts by weight, per 100 parts by weight of the acrylic resin, of an ultraviolet absorbent.

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DESCRIPTION

SURFACE-PROTECTED TRANSPARENT PLASTIC COMPOSITE MATERIAL

5 Detailed Description of the Invention

Field of the Invention

The present invention relates to a surface-protected transparent plastic composite material. More specifically, it relates to a transparent plastic composite material which comprises a layer made mainly of an acrylic resin and a cured product layer of an organosiloxane resin that are consecutively laminated on a transparent plastic substrate and which is remarkably improved in abrasion resistance and peel resistance.

15 Prior Art of the Invention

Plastic materials are widely used in various fields owing to characteristic features such as impact resistance, lightweight properties and processability. Above all, an acrylic resin, a polycarbonate resin, a styrene resin, etc., that are transparent plastics are widely used as a substitute for glass. However, these resins have a defect that they are poor in abrasion resistance, liable to suffer scratching on a surface and liable to be eroded with a solvent.

In recent years, there is a tendency to apply a transparent plastic sheet to a window glass, particularly, an automobile window glass, as an organic glass while utilizing the lightweight properties and safety thereof. When a transparent plastic sheet is applied to such a use, for example, a windshield, it is required to prevent the occurrence of scratching caused during the operation of a wiper, and when it is applied to a side window, it is required to prevent the occurrence of scratching during the elevating of the

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window up and down. For such applications, the transparent plastic sheet is required to have high-level abrasion resistance equivalent to that of glass.

Further, automobile window glasses are exposed to various environments outdoors for a long time, and they are required to satisfy such high-level abrasion resistance and weatherability as those of glass.

For overcoming the above drawbacks, there have been already made a variety of proposals to improve a plastic substrate in abrasion resistance by forming an adhesive layer on the plastic substrate as required and coating the surface thereof with a cured coating of a siloxane. For example, JP-A-51-2736 and JP-A-55-94971 describe a coating composition comprising a trihydroxysilane partial condensate and colloidal silica. Further, JP-A-48-26822 and JP-A-51-33128 describe a coating composition comprising, as a main component, a partial condensate of an alkyltrialkoxysilane and a tetraalkoxysilane. When a laminate is obtained by coating a transparent plastic substrate with the coating composition comprising a trihydroxysilane partial condensate and colloidal silica or the coating composition comprising, as a main component, a partial condensate of an alkyltrialkoxysilane and a tetraalkoxysilane to form a cured coating film, the laminate has good abrasion resistance to some extent. When it is applied to the field of an automobile window glass, however, the abrasion resistance thereof is not satisfactory, and it is demanded to improve the above coating compositions further in abrasion resistance.

Further, JP-A-63-278979 and JP-A-1-306476 describe a coating composition prepared by adding colloidal silica to a condensate of an alkyltrialkoxysilane and a tetraalkoxysilane. However, the above coating

composition has been developed mainly for surface protection of inorganic materials such as natural marble and metals, and it does not ensure the formation of a protective layer having good adhesion on a plastic substrate. When the coating composition disclosed in the above patent publications was actually used to form a coating on a polycarbonate resin through an adhesive layer, a coating layer underwent cracking during the curing thereof under heat or no sufficient abrasion resistance was attained, since the amount ratio of the colloidal silica, trialkoxysilane and tetraalkoxysilane had not been fully studied for formation of a protective layer on a plastic. Further, even if some compositions are free from the occurrence of cracking and attains sufficient abrasion resistance, a coating formed thereof has a problem that the coating layer undergoes cracking since it undergoes a complete curing reaction when reheated or immersed in boiling water and since the thermal expansion coefficient of a plastic substrate and the counterpart of the coating layer differs. It has been therefore demanded to further improve the above composition for applying it to a plastic substrate.

In a coated plastic molded material formed by coating a polycarbonate resin substrate surface with an adhesive layer (primer layer) and a cured siloxane resin coating film, further, it has been proposed in many ways to incorporate an ultraviolet absorbent into the adhesive layer so that the coated plastic molded material is improved in weatherability. For example, such proposals are made in JP-A-61-86259, JP-A-2-16048, JP-A-2-16129, JP-A-4-106161 and JP-A-5-255526.

The weatherability is improved by incorporating an ultraviolet absorbent into the adhesive layer as described above. However, some ultraviolet absorbents

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bleed into a top layer coating liquid during formation of a top layer coating. As a result, the top coating layer may decrease in abrasion resistance, or an incorporated ultraviolet absorbent may bleed out during exposure outdoors for a long time, so that there may be caused a problem that a coating film peels or that the polycarbonate resin molded material undergoes yellowing. It is therefore necessary to be careful in selecting an ultraviolet absorbent.

10 Problems to be solved by the Invention

It is a first object of the present invention to provide a transparent plastic composite material that is surface-protected with a cured coating film having unconventional high-level abrasion resistance.

15 It is a second object of the present invention to provide a transparent plastic composite material that is free from cracking of a cured coating layer under environmental conditions during outdoor exposure and that is free from bleeding-out of an ultraviolet
20 absorbent.

It is a third object of the present invention to provide a transparent plastic composite material comprising a transparent plastic substrate and a coating layer, in which the coating layer formed on the
25 transparent plastic substrate does not peel, and the transparent plastic substrate is almost free of yellowing and deterioration, during use for a long period of time.

It is another object of the present invention to
30 provide a transparent plastic composite material that is light in weight, can be used for a long period of time without losing its transparency and is therefore suitable for a window glass in transportation machines and equipment for which a decrease in weight is demanded,

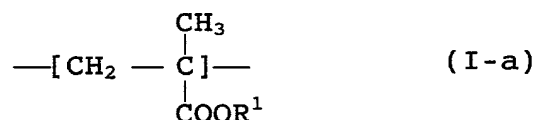
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such as automobiles, train cars, aircrafts, and the like.

For achieving the above objects of the present invention, the present inventors have accordingly made diligent studies. As a result, it has been found that a composite material formed by stacking an acrylic resin coating layer (first layer) having a specific composition on a transparent plastic substrate surface and stacking an organosiloxane resin cured layer (second layer) having a specific composition on the surface of the above coating layer has surface properties including an unconventional high-level abrasion resistance, is excellent in peel resistance and remarkably free from cracking under environmental conditions during outdoor exposure, retains transparency during use for a long period of time and is almost free from yellowing and deterioration against ultraviolet light. The present invention has been accordingly arrived at.

Means to Solve the Problems

That is, according to the present invention, there is provided a surface-protected plastic composite material comprising a transparent plastic, a coating layer (I) as a first layer stacked on the transparent plastic substrate and a thermally cured coating layer (II) as a second layer stacked on the first layer, the coating layer (I) being formed of a resin composition containing at least 50 % by weight, based on the resin content thereof, of an acrylic resin which is an acrylic resin containing at least 50 mol% of recurring unit of the following formula (I-a),



wherein R^1 is an alkyl group having 1 to 4 carbon atoms,

(A) colloidal silica (component a),

- carbon atoms and is substituted with at least one group selected from the class consisting of methacryloxy, amino, glycidoxy and 3,4-epoxycyclohexyl and R³ is an alkyl group having 1 to 4 carbon atoms, and (C) a hydrolysis condensate (component c) of a tetraalkoxysilane of the following formula (II-2),



wherein R⁴ is an alkyl group having 1 to 4 carbon atoms, the organosiloxane resin containing 5 to 45 % by weight of the component a, 50 to 80 % by weight, as 20 R²SiO_{3/2}, of the component b and 2 to 30 % by weight, as SiO₂, of the component c.

25 To explain the transparent plastic composite material of the present invention simply, it is constituted of a transparent plastic substrate, a coating layer (first layer) made of a specific acrylic resin and formed on the surface thereof and a cured
30 coating layer (second layer) made of a specific organosiloxane resin composition and formed on the surface of the first layer. The first layer and the second layer may be formed on one surface, or they may be formed on both the surfaces of the transparent

plastic substrate.

In the present specification, the transparent plastic substrate, the coating layer (first layer) and the cured coating layer (second layer) constituting the transparent plastic composite material will be specifically explained in detail in the order of the transparent plastic substrate, the coating layer (first layer) and the cured coating layer (second layer).

The transparent plastic substrate for constituting the transparent plastic composite material of the present invention is a transparent plastic molded material having the form of a film, a sheet or a board. The term "transparent" means that the plastic molded material has a haze value of 10 % or less, preferably 8 % or less, in terms of a transparency. The transparent plastic substrate has a thickness of 0.001 to 10 mm, preferably 0.02 to 8 mm, and when the plastic forming the transparent plastic substrate is an aromatic polycarbonate resin, a transparent plastic substrate having a thickness of 0.1 to 8 mm is used. The above thickness is not necessarily required to be uniform, and the transparent plastic substrate may have a moderate change in thickness.

The plastic forming the transparent plastic substrate may be any plastic so long as it has the above transparency and the above form. Specifically, the plastic includes (a) an aromatic polycarbonate resin; (b) acrylic resins such as polymethyl methacrylate; (c) polyester resins such as polyethylene terephthalate, polybutylene terephthalate and poly(ethylene-2,6-naphthalate); (d) polystyrene; (e) polypropylene; (f) polyarylate; and (g) polyether sulfone. In view of usefulness as a substrate having adhesion to the first layer and having excellent abrasion resistance, (a) a

polycarbonate resin and (b) acrylic resins such as polymethyl methacrylate are preferred, and (a) a polycarbonate resin is particularly preferred.

The aromatic polycarbonate resin suitable for the transparent plastic substrate will be explained below.

The polycarbonate resin for use is generally obtained from a dihydric phenol and a carbonate precursor by an interfacial polycondensation method or a melt polymerization method. Typical examples of the dihydric phenol used in this case include hydroquinone, resorcinol, 4,4'-dihydroxydiphenyl, bis(4-hydroxyphenyl)methane, bis{(4-hydroxy-3,5-dimethyl)phenyl}methane, 1,1-bis(4-hydroxyphenyl)ethane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, 2,2-bis(4-hydroxyphenyl)propane (generally called "bisphenol A"), 2,2-bis{(4-hydroxy-3-methyl)phenyl}propane, 2,2-bis{(4-hydroxy-3,5-dimethyl)phenyl}propane, 2,2-bis{(3,5-dibromo-4-hydroxy)phenyl}propane, 2,2-bis{(3-isopropyl-4-hydroxy)phenyl}propane, 2,2-bis{(4-hydroxy-3-phenyl)phenyl}propane, 2,2-bis(4-hydroxyphenyl)butane, 2,2-bis(4-hydroxyphenyl)-3-methylbutane, 2,2-bis(4-hydroxyphenyl)-3,3-dimethylbutane, 2,4-bis(4-hydroxyphenyl)-2-methylbutane, 2,2-bis(4-hydroxyphenyl)pentane, 2,2-bis(4-hydroxyphenyl)-4-methylpentane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 1,1-bis(4-hydroxyphenyl)-4-isopropylcyclohexane, 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane, 9,9-bis(4-hydroxyphenyl)fluorene, 9,9-bis{(4-hydroxy-3-methyl)phenyl}fluorene, α,α' -bis(4-hydroxyphenyl)-o-diisopropylbenzene, α,α' -bis(4-hydroxyphenyl)-m-diisopropylbenzene, α,α' -bis(4-hydroxyphenyl)-p-diisopropylbenzene, 1,3-bis(4-hydroxyphenyl)-5,7-dimethyladamantane, 4,4'-dihydroxydiphenylsulfone, 4,4'-dihydroxydiphenyl sulfoxide, 4,4'-dihydroxydiphenyl

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sulfide, 4,4'-dihydroxydiphenyl ketone, 4,4'-
dihydroxydiphenyl ether and 4,4'-dihydroxydiphenyl ester.
Of these, 2,2-bis(4-hydroxyphenyl)alkanes are preferred,
and bisphenol A is particularly preferred. The above
5 dihydric phenols may be used alone or in combination.

The carbonate precursor is selected from carbonyl
halides, carbonate esters or haloformates, and specific
examples thereof include phosgene, diphenyl carbonate
and dihaloformate of a dihydric phenol.

10 When the above dihydric phenol and the carbonate
precursor are allowed to react by an interfacial
polycondensation method or a melt polymerization method
to produce a polycarbonate resin, a catalyst, a terminal
stopper and an antioxidant for the dihydric phenol may
15 be used as required. Further, the polycarbonate resin
may be a branched polycarbonate resin formed by
copolymerization of trifunctional or higher
polyfunctional aromatic compounds or may be a polyester
carbonate resin formed by copolymerization of aromatic
20 or aliphatic difunctional carboxylic acids, and it may
be also a mixture of two or more of obtained
polycarbonate resins.

The reaction by an interfacial polycondensation
method is generally a reaction between a dihydric phenol
25 and phosgene, and the reaction is carried out in the
presence of an acid binder and an organic solvent. The
acid binder is selected, for example, from alkali metal
hydroxides such as sodium hydroxide and potassium
hydroxide or amine compounds such as pyridine. The
30 organic solvent is selected, for example, from
halogenated hydrocarbons such as methylene chloride and
chlorobenzene. For promoting the reaction, there may be
used a catalyst that is selected, for example, from
tertiary amines such as triethylamine, tetra-n-

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butylammonium bromide and tetra-n-butylphosphonium bromide, quaternary ammonium compounds or quaternary phosphonium compounds. In this case, preferably, the reaction temperature is generally 0 to 40°C, the
5 reaction time period is approximately 10 minutes to 5 hours, and the pH during the reaction is maintained at 9 or more.

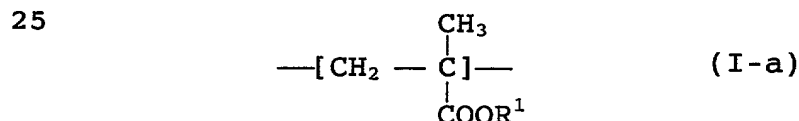
In the above interfacial polymerization method, generally, a terminal stopper is used. The terminal
10 stopper is selected from monofunctional phenols. Monofunctional phenols are generally used as a terminal stopper for adjusting molecular weights, and an obtained polycarbonate resin has terminals blocked with groups from the monofunctional phenols, so that the
15 polycarbonate resin has excellent thermal stability over any other resin. Examples of the above monofunctional phenols include phenol, p-tert-butylphenol, p-cumylphenol and isooctylphenol. Of these, p-tert-butylphenol is preferred.

20 The reaction by a melt polymerization method is generally an ester exchange reaction between a dihydric phenol and a carbonate ester, and the reaction is carried out by a method in which a dihydric phenol and a carbonate ester are mixed under heat in the presence of
25 an inert gas and an alcohol or a phenol being formed is distilled off. Although differing depending upon the boiling point of the formed alcohol or phenol or the like, the reaction temperature is generally in the range of from 120°C to 350°C. At a later stage of the reaction,
30 the pressure in the reaction system is reduced approximately to 1,300 Pa to 13 Pa (10 to 0.1 Torr) to easily distill the formed alcohol or phenol off. The reaction time period is generally approximately 1 to 4 hours.

The obtained polycarbonate resin preferably has a specific viscosity in the range of 0.25 to 0.6, preferably 0.3 to 0.55 when 0.7 g of the polymer thereof is dissolved in 100 ml of methylene chloride and measured for a specific viscosity at 20°C. A polycarbonate resin substrate having a desired thickness, used in the present invention, can be obtained by a method in which the polycarbonate resin obtained by the above production method is molded by a method for producing a general film or sheet, for example, by a melt extrusion method using a T-die extruder.

In the transparent plastic composite material of the present invention, as a first layer, the coating layer (I) formed of a resin composition containing at least 50 % by weight, based on the resin content thereof, of an acrylic resin is stacked on the surface of the above transparent plastic substrate. The coating layer (I) is interposed between the transparent plastic substrate and the thermally cured coating layer (II) and works to strongly bond these two elements.

The acrylic resin as a main component of the coating layer (I) as a first layer is a polymer containing at least 50 mol%, based on the total of recurring units, of recurring units of the following formula (I-a),



wherein R¹ is an alkyl group having 1 to 4 carbon atoms.

The above acrylic resin preferably contains at least 60 mol% of recurring units of the above formula (I-a), and more preferably contains at least 70 mol% thereof. An acrylic resin containing less than 50 mol% of recurring units of the above formula (I-a) is

undesirable since it is poor in adhesion between the transparent plastic substrate and the thermally cured coating layer (II) as a second layer.

The above acrylic resin is a polymer obtained by polymerizing at least 50 mol% of an alkyl methacrylate monomer and not more than 50 mol% of a vinyl monomer. The alkyl methacrylate monomer specifically includes methyl methacrylate, ethyl methacrylate, propyl methacrylate and butyl methacrylate, and these monomers may be used alone or in combination. Of these, methyl methacrylate and ethyl methacrylate are preferred, and methyl methacrylate in particular is excellent.

The other vinyl monomer is a monomer copolymerizable with the alkyl methacrylate monomer, and it is preferably selected from acrylic acid, methacrylic acid or derivatives of these in view of adhesion or durability such as weatherability. Specifically, the vinyl monomer includes acrylic acid, methacrylic acid, acrylic acid amide, methacrylic acid amide, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, 2-ethylhexyl methacrylate, dodecyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, N,N-diethylaminoethyl methacrylate, glycidyl methacrylate, 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane and 3-methacryloxypropylmethyldimethoxysilane. These monomers may be used alone or in combination. Further, the acrylic resin may be a mixture of acrylic resins.

The above acrylic resin is preferably a thermosetting resin, and for this reason, the acrylic resin desirably contains at least 0.01 mol% but less than 50 mol% of a vinyl monomer having a crosslinking reactive group. The vinyl monomer having a crosslinking

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methacryloxypropyltriethoxysilane and 3-methacryloxypropylmethyldimethoxysilane.

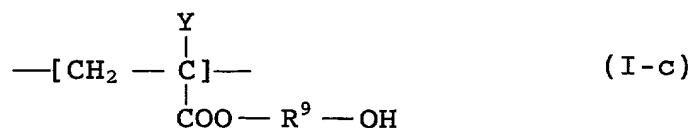
10 The above acrylic resin having a molecular weight in the above range is preferred since it fully exhibits performances of adhesion and strength as a first layer.

In the present invention, the acrylic resin for forming the coating layer (I) to be stacked on the surface of the transparent plastic substrate can be an acrylic copolymer resin to be described later. The acrylic copolymer resin is a preferred embodiment as an acrylic resin for forming the coating layer (I).

$$30 \quad \begin{array}{c} \text{X} \\ | \\ \text{---}[\text{CH}_2 - \text{C}] \text{---} \\ | \\ \text{COO} - \text{R}^5 - \text{Si}(\text{CH}_3)_n(\text{OR}^6)_{3-n} \end{array} \quad (\text{I-b})$$

wherein X is a hydrogen atom or methyl, R⁵ is an alkylene group having 2 to 5 carbon atoms, R⁶ is an alkyl group having 1 to 4 carbon atoms and n is an

integer of 0 or 1,



- 5 wherein Y is a hydrogen atom or methyl and R⁹ is an alkylene group having 2 to 5 carbon atoms.

The above acrylic copolymer resin has a (I-a):[(I-b) + (I-c)] molar ratio of the units in the range of from 99.5:0.5 to 50:50.

- 10 In the above acrylic copolymer resin, the (I-a):[(I-b) + (I-c)] molar ratio of the units is preferably in the range of from 99:1 to 60:40, more preferably from 97:3 to 70:30.

- The above acrylic copolymer resin can be obtained by
- 15 copolymerizing the above alkyl methacrylate monomer together with an acrylate (or methacrylate) monomer having an alkoxysilyl group and/or an acrylate (or methacrylate) monomer having a hydroxy group as comonomer(s). The acrylate (or methacrylate) monomer
- 20 having an alkoxysilyl group, which gives the recurring units of the above formula (I-b), specifically includes 3-methacryloxypropyltrimethoxysilane, 3-acryloxypropyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane, 3-acryloxypropyltriethoxysilane, 3-
- 25 methacryloxypropylmethyldimethoxysilane and 3-acryloxypropylmethyldimethoxysilane. Preferred are 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane and 3-
- 30 methacryloxypropylmethyldimethoxysilane, and 3-methacryloxypropyltrimethoxysilane is particularly preferred.

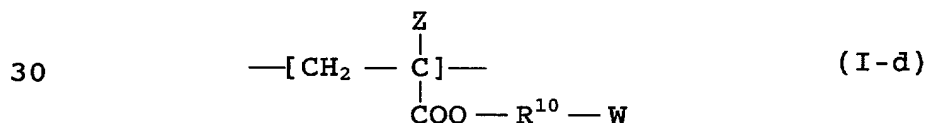
When the acrylic copolymer resin obtained by copolymerization of the acrylate (or methacrylate)

monomer having an alkoxysilyl group and the alkyl methacrylate monomer is used, the adhesion to the organosiloxane resin thermally cured layer as a second layer is improved, the transparent plastic composite material is further improved in durability against hot water, and the copolymer obtained by copolymerization in the above amount ratio does not easily undergo gelling, so that it has an excellent shelf life. It is assumed that the above acrylic copolymer resin is structurally similar to the second layer and has affinity thereto since it has an alkoxysilyl group, and that the adhesion thereof to the second layer is hence more improved.

The acrylate (or methacrylate) monomer having a hydroxy group, which gives recurring units of the above formula (I-c), specifically includes 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate and 2-hydroxypropyl methacrylate. Of these, 2-hydroxyethyl methacrylate is preferred.

Other preferred embodiment of the acrylic copolymer resin will be explained below. The "other embodiment" is that the above acrylic copolymer resin is a resin formed by copolymerization of an acrylate (or methacrylate) further having an ultraviolet absorbent residue.

That is, the acrylic copolymer resin as other embodiment is an acrylic copolymer resin containing 0.3 to 40 mol%, based on the total units of the above formulae (I-a) and [(I-b) + (I-c)], of units of the following formula (I-d),



wherein Z is a hydrogen atom or methyl, R^{10} is an alkylene group having 2 to 5 carbon atoms and W is an ultraviolet absorbent residue.

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component for the coating layer (I), the amount thereof can be decreased. That is, when a large amount of an ultraviolet absorbent is incorporated into an acrylic resin, the ultraviolet absorbent may bleed out, and such a drawback can be decreased.

The acrylic resin in the coating layer (I) in the present invention may contain a hydrolysis condensate of an alkoxysilane. That is, the coating layer (I) may be a layer formed of a mixture of the above acrylic resin with a hydrolysis condensate of an alkoxysilane of the following formula (I-e) in which the acrylic resin:hydrolysis condensate amount ratio by weight is in the range of from 99:1 to 60:40, preferably from 97:3 to 70:30. The above amount ratio is expressed by taking the amount of the hydrolysis condensate as $R^7_r\text{-SiO}_{4-r/2}$.



wherein R^7 is an alkyl group having 1 to 4 carbon atoms, a vinyl group or an alkyl group which is substituted with one or more groups selected from the class consisting of methacryloxy, amino, glycidoxy and 3,4-epoxycyclohexyl and has 1 to 3 carbon atoms, R^8 is an alkyl group having 1 to 4 carbon atoms, and r is an integer of 0 to 2.

Examples of the alkoxysilane of the above formula (I-e) include tetramethoxysilane, tetraethoxysilane, tetra-n-propoxysilane, tetraisopropoxysilane, tetra-n-butoxysilane, tetraisobutoxysilane, methyltrimethoxysilane, methyltriethoxysilane, ethyltrimethoxysilane, isobutyltrimethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, γ -methacryloxypropyltrimethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane, γ -aminopropyltrimethoxysilane, γ -aminopropyltriethoxysilane,

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N- β (aminoethyl)- γ -aminopropyltrimethoxysilane, N- β (aminoethyl)- γ -aminopropyltriethoxysilane, dimethyldimethoxysilane, vinylmethyldimethoxysilane, 3-methacryloxypropylmethyldimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane and 3-aminopropylmethyldiethoxysilane. Of these, alkyltrialkoxysilanes are preferred, and methyltrimethoxysilane and methyltriethoxysilane are particularly preferred. These may be used alone or in combination.

The above hydrolysis condensate of an alkoxysilane can be obtained by hydrolysis condensation of an alkoxysilane of the above formula (I-e) under acidic conditions using water generally in an amount, per equivalent weight of the alkoxy group of the alkoxysilane, of 0.2 to 4 equivalent weights, preferably 0.5 to 2 equivalent weights, more preferably 1 to 1.5 equivalent weight at 20 to 40°C for 1 hour to several days. The hydrolysis condensation uses an acid, and the acid includes inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, nitrous acid, perchloric acid and sulfamic acid, and organic acids such as formic acid, acetic acid, propionic acid, butyric acid, oxalic acid, succinic acid, maleic acid, lactic acid and p-toluenesulfonic acid. Volatile acids such as acetic acid, hydrochloric acid, etc., are preferred. When an inorganic acid is used, the acid is used generally in a concentration of 0.0001 to 2N, preferably 0.001 to 0.1 N, and when an organic acid is used, the acid is used in an amount in the range, per 100 parts by weight of the alkoxysilane, of from 0.1 to 50 parts by weight, preferably from 1 to 30 parts by weight.

When the above alkoxysilane hydrolysis condensate is

incorporated, preferably, a catalyst is added for promoting the condensation of the alkoxysilane hydrolysis condensate. The catalyst includes alkali metal salts, such as lithium salts, sodium salts and potassium salts, of aliphatic carboxylic acids such as formic acid, propionic acid, butyric acid, lactic acid, tartaric acid and succinic acid, and quaternary ammonium salts such as benzyltrimethylammonium salt, tetramethylammonium salt and tetraethylammonium salt.

5 Sodium acetate, potassium acetate and benzyltrimethylammonium acetate are preferred. The amount of the above catalyst per 100 parts by weight of the alkoxysilane hydrolysis condensate is preferably in the range of from 0.5 to 10 parts by weight, more preferably from 1 to 5 parts by weight.

When the hydrolysis condensate of the above formula (I-e) is incorporated, a melamine resin may be further incorporated into the acrylic resin in the coating layer (I) in the present invention. When incorporated, the melamine resin can improve physical properties such as adhesion between the transparent plastic substrate and the cured coating layer (II). Examples of the melamine resin to be incorporated include a complete alkyl type methylated melamine typified by

20 hexamethoxymethylmelamine, hexamethoxymethylmelamine of which the methoxymethyl group is partially converted to a methylol group, an imino group or a butoxymethyl group, and a complete alkyl type butylated melamine typified by hexabutoxymethylmelamine. Specifically, the above

25 melamine resin includes Cymel 300, Cymel 301, Cymel 303, Cymel 350, Cymel 370, Cymel 771, Cymel 325, Cymel 712, Cymel 202, Cymel 207 and Cymel 212 supplied by Mitsui Cytec K.K. Of these resins, a complete alkyl type methylated melamine typified by hexamethoxymethylated

melamine is preferably used. Such a resin specifically includes Cymel 300 (average polymerization degree: 1.35, ratio of methoxymethyl group: 95 % or more), Cymel 301 (average polymerization degree: 1.5, ratio of methoxymethyl group: 90 % or more), Cymel 303 (average polymerization degree: 1.7, ratio of methoxymethyl group: 90 % or more) and Cymel 350 (average polymerization degree: 1.6, ratio of methoxymethyl group: 85 % or more). These melamine resins are used alone or in combination. When the melamine resin is used, preferably, an acid catalyst is further used for promoting the curing of the above melamine resin. The acid catalyst includes inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, nitrous acid, perchloric acid and sulfamic acid, and organic acids such as maleic acid, formic acid, acetic acid, propionic acid, butyric acid, oxalic acid, succinic acid, lactic acid, benzenesulfonic acid and p-toluenesulfonic acid. Preferably, a volatile acid having a sufficient acidity such as maleic acid, benzenesulfonic acid or p-toluenesulfonic acid is used. The amount of the above acid catalyst per 100 parts by weight of the melamine resin is preferably in the range of from 0.5 to 10 parts by weight, preferably from 1 to 5 parts by weight.

The amount of the melamine resin per 100 parts by weight of the total of the acrylic resin and the hydrolysis condensate of the compound of the above formula (I-e) is preferably 1 to 20 parts by weight, more preferably 3 to 15 parts by weight. When they are mixed in the above amount range, the coating layer (I) can maintain excellent adhesion to the transparent plastic substrate and the cured coating layer (II).

The acrylic resin in the coating layer (I) in the

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present invention may contain a light stabilizer and an ultraviolet absorbent for weatherability, particularly, photostability, of the transparent plastic substrate. These can be selected from those that are generally used as a light stabilizer and an ultraviolet absorbent for plastics, and above all, desirable are those that do not impair the transparency of the transparent plastic substrate.

Examples of the above light stabilizer include hindered amines such as bis(2,2,6,6-tetramethyl-4-piperidyl)carbonate, bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, 4-benzoyloxy-2,2,6,6-tetramethylpiperidine, 4-octanoyloxy-2,2,6,6-tetramethylpiperidine, bis(2,2,6,6-tetramethyl-4-piperidyl)diphenylmethane-p,p'-dicarbamate, bis(2,2,6,6-tetramethyl-4-piperidyl)benzene-1,3-disulfonate and bis(2,2,6,6-tetramethyl-4-piperidyl)phenyl phosphite, and nickel complexes such as nickel bis(octylphenyl)sulfide, nickel complex-3,5-di-t-butyl-4-hydroxybenzyl phosphoric acid monoethylate and nickel dibutyl dithiocarbamate. These light stabilizers may be used alone or in combination, and the amount thereof per 100 parts by weight of the acrylic resin in the coating layer (I) is preferably 0.1 to 50 parts by weight, more preferably 0.5 to 10 parts by weight.

Examples of the ultraviolet absorbent include benzophenones such as 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-octoxybenzophenone, 4-benzyloxy-2-hydroxybenzophenone, 4-dodecyloxy-2-hydroxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone and bis(5-benzoyl-4-hydroxy-2-methoxyphenyl)methane, benzotriazoles such as 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-5'-

t-octylphenyl)benzotriazole, 2-(3'-t-butyl-5'-methyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-di-t-butyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-di-t-pentyl-2'-hydroxyphenyl)benzotriazole, 2-(3'-t-butyl-5'-methyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3',5'-di-t-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(2H-benzotriazol-2-yl)-4-methyl-6-3,4,5,6,-tetrahydrophthalimidyl)phenol and bis(3-2H-benzotriazol-2-yl-2-hydroxy-5-t-octylphenyl)methane, cyanoacrylates such as ethyl-2-cyano-3,3-diphenyl acrylate and 2-ethylhexyl-2-cyano-3,3-diphenyl acrylate, salicylates such as phenyl salicylate and p-octylphenyl salicylate, benzylidene malonates such as diethyl-p-methoxybenzylidene malonate and bis(2-ethylhexyl)benzylidene malonate, and triazines such as 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-hexyloxyphenol. These absorbents may be used alone or in combination.

The ultraviolet absorbent is preferably an ultraviolet absorbent that is soluble in a solvent mixture having a specific composition only up to a specific limit of its amount ratio. When an ultraviolet absorbent having such a feature is used, it is not eluted in a coating solution for the cured coating layer (II) during the application of the coating solution for the cured coating layer (II), so that the abrasion resistance of the cured coating layer (II) is not impaired, and there can be obtained a transparent plastic composite material excellent in abrasion resistance and weatherability. That is, the ultraviolet absorbent is preferably selected from ultraviolet absorbents that have a solubility of 1.5 g/L or less when measured in solvent mixture containing 100 parts by weight of isopropanol, 30 parts by weight of methanol and 15 parts by weight of water at 25°C.

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Specific examples of the above ultraviolet absorbent include benzophenones such as 4-benzyloxy-2-hydroxybenzophenone and bis(5-benzoyl-4-hydroxy-2-methoxyphenyl)methan, benzotriazoles such as 2-(2'-hydroxy-5'-t-octylphenyl)benzotriazole, 2-(3'-t-butyl-5'-methyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-di-t-butyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-di-t-pentyl-2'-hydroxyphenyl)benzotriazole, 2-(3'-t-butyl-5'-methyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3',5'-di-t-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(2H-benzotriazol-2-yl)-4-methyl-6-3,4,5,6-tetrahydrophthalimidylphenol and bis(3-2H-benzotriazol-2-yl-2-hydroxy-5-t-octylphenyl)methane and triazines such as 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-hexyloxyphenol.

Further, when the plastic forming the transparent plastic substrate is an aromatic polycarbonate resin, the ultraviolet absorbent is particularly preferably selected from 2-(3'-t-butyl-5'-methyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3',5'-di-t-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-5'-t-octylphenyl)benzotriazole or 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-hexyloxyphenol.

The amount of the above ultraviolet absorbent per 100 parts by weight of the acrylic resin in the coating layer (I) is 0.7 to 100 parts by weight, preferably 3 to 60 parts by weight, more preferably 5 to 50 parts by weight. Particularly, when the acrylic resin is an acrylic copolymer resin having the ultraviolet absorbent residue shown in the above formula (I-d), the above ultraviolet absorbent is incorporated such that the total sum of the weight of the units of the above formula (I-d) and the ultraviolet absorbent comes into the above range. That is, when the recurring units of

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the above formula (I-d) are contained as an acrylic copolymer resin in addition to the ultraviolet absorbent incorporated, the amount of the ultraviolet absorbent in the present specification is calculated by including the amount of the ultraviolet absorbent residue of the formula (I-d) (i.e., total amount of W).

In the present invention, generally and preferably, the coating layer (I) as a first layer is formed on the surface of the transparent plastic substrate by a method in which a solution of the above acrylic resin in a proper solvent is coated and the solvent is removed. That is, the above acrylic resin component (including the acryl copolymer resin and other resin component) is dissolved in a volatile solvent that is free from reacting with the transparent plastic as a substrate and dissolving said transparent plastic, together with the light stabilizer and/or the ultraviolet absorbent as required, to prepare a coating composition, the coating composition is applied onto the surface of the transparent plastic substrate, and the solvent is removed by heating or the like. After the removal of the solvent, it is preferred to further heat the coating to 40 to 140°C as required, to crosslink crosslinking groups.

The above solvent includes ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone, ethers such as tetrahydrofuran, 1,4-dioxane and 1,2-dimethoxyethane, esters such as ethyl acetate and ethoxyethyl acetate, alcohols such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-ethoxyethanol, 4-methyl-2-pentanol and 2-butoxyethanol, hydrocarbons such as n-hexane, n-heptane, isooctane, benzene, toluene, xylene, gasoline, light oil and kerosene; acetonitrile,

nitromethane and water. These may be used alone or in combination. In the above coating composition, the concentration of a solid component formed of the coating resin is preferably 1 to 50 % by weight, more preferably 3 to 30 % by weight.

The above coating composition is applied to the plastic substrate by a method that can be properly selected from a bar coating method, a dip coating method, a flow coating method, a spray coating method, a spin coating method, a roller coating method, or the like depending upon the size and form of the substrate to be coated therewith. In the substrate coated with the above coating composition, the solvent is dried and removed generally at a temperature between room temperature and the heat distortion temperature of the substrate, and further, if necessary, the substrate is heated to 40 to 140°C to crosslink crosslinking groups after the removal of the solvent, whereby there is obtained the transparent plastic substrate on which the coating layer (I) as a first layer is stacked.

The thickness of the coating layer (I) as a first layer can be any thickness so long as the coating layer (I) can fully bond the transparent plastic substrate and the second layer and can hold necessary amounts of the above various additives. The thickness above is preferably 0.1 to 10 μm , more preferably 1 to 5 μm .

When the first layer made of the coating layer mainly containing the above acrylic resin is formed, the adhesion between the second layer and the transparent plastic substrate is improved, and there can be obtained a transparent plastic composite material excellent in abrasion resistance and weatherability.

In the transparent plastic composite material of the present invention, the thermally cured coating layer

(II) made of an organosiloxane resin having a specific composition as a second layer is further stacked on the surface of the coating layer (I) stacked on the surface of the above transparent plastic substrate.

5 The above second layer is a thermally cured coating layer (II) made of an organosiloxane resin formed from the following components a, b and c,

(A) colloidal silica (component a)

(B) a hydrolysis condensate of a trialkoxysilane of the
10 following formula (II-1) (component b),



wherein R^2 is an alkyl group having 1 to 4 carbon atoms, a vinyl group or an alkyl group which is substituted with one or more groups selected from
15 methacryloxy, amino, glycidoxy and 3,4-epoxycyclohexyl and has 1 to 3 carbon atoms, and R^3 is an alkyl group having 1 to 4 carbon atoms, and

(C) a hydrolysis condensate of a tetraalkoxysilane of the following formula (II-2) (component c),



20 wherein R^4 is an alkyl group having 1 to 4 carbon atoms,

the organosiloxane resin being a resin composition containing 5 to 45 % by weight of the component a, 50 to
25 80 % by weight, as $\text{R}^2\text{SiO}_{3/2}$, of the component b and 2 to 30 % by weight, as SiO_2 , of the component c.

The second layer is preferably formed from a coating composition containing an organosiloxane resin solid component formed from the above (A) colloidal silica
30 (component a), (B) hydrolysis condensate of a trialkoxysilane (component b) and (C) hydrolysis condensate of a tetraalkoxysilane (component c), an acid, a curing catalyst and a solvent. Each of the above components a, b and c will be explained below.

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The colloidal silica as component a refers to a colloidal dispersion of fine silica particles having a diameter of 5 to 200 nm, preferably 5 to 40 nm, in water or an organic solvent. While the colloidal silica may be any type such as a type of a dispersion in water and a type of dispersion in an organic solvent, it is preferred to use a dispersion in water. The colloidal silica specifically includes Snowtex 0 supplied by Nissan Chemical Industries, Ltd. as a commercial product that is a dispersion in an acidic aqueous solution, Snowtex 30 and Snowtex 40 supplied by Nissan Chemical Industries, Ltd. and Cataloid S30 and Cataloid S40 supplied by Catalysts & Chemicals Ind. Co. Ltd. as commercial products that are dispersions in a basic aqueous solution, and MA-ST, IPA-ST, NBA-ST, IBA-ST, EG-ST, XBA-ST, NPC-ST and DMAC-ST supplied by Nissan Chemical Industries, Ltd. as commercial products that are dispersions in an organic solvent.

The hydrolysis condensate of a trialkoxysilane as component b is a product formed by hydrolysis condensation of a trialkoxysilane of the above formula (II-1).

Examples of the above trialkoxysilane includes methyltrimethoxysilane, methyltriethoxysilane, ethyltrimethoxysilane, isobutyltrimethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, γ -methacryloxypropyltrimethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane, γ -aminopropyltrimethoxysilane, γ -aminopropyltriethoxysilane, N- β (aminoethyl) γ -aminopropyltrimethoxysilane and N- β (aminoethyl) γ -aminopropyltriethoxysilane. These may be used alone or in combination.

For obtaining a coating composition to form a

coating layer having excellent abrasion resistance in particular, preferably, methyltrialkoxysilane constitutes at least 70 % by weight of the entire trialkoxysilanes, and more preferably,

- 5 methyltrialkoxysilane constitutes substantially the entire trialkoxysilanes. For the purpose of improving adhesion and exhibiting functions such as hydrophilicity and water repellency, a small amount of trialkoxysilanes other than the methyltrialkoxysilane may be added.

- 10 The hydrolysis condensate of a tetraalkoxysilane as component (c) is a product formed by hydrolysis condensation of a tetraalkoxysilane of the above formula (II-2). Examples of the above tetraalkoxysilane include tetramethoxysilane, tetraethoxysilane, tetra-n-
15 propoxysilane, tetraisopropoxysilane, tetra-n-butoxysilane and tetraisobutoxysilane.

Tetramethoxysilane and tetraethoxysilane are preferred. These tetraalkoxysilanes may be used alone or in combination.

- 20 The components b and c is a mixture of hydrolysis products of part or the whole of the above alkoxysilanes and a condensation product of part or the whole of the above hydrolysis products, and these can be obtained by a sol-gel reaction.

- 25 For preparing the organosiloxane solid component formed of the components a to c, it is preferred to prepare the organosiloxane solid component through the following processes (1) and (2), since no precipitate is formed and since the cured layer (II) having superior
30 abrasion resistance can be obtained.

Process (1): The trialkoxysilane of the above formula (II-1) is allowed to undergo a hydrolysis condensation in a colloidal silica dispersion under an acidic condition.

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When a dispersion of the colloidal silica in water is used, the dispersion supplies water required for the hydrolysis of the trialkoxysilane. Additional water may be added as required. In this case, the water is used generally in an amount of 1 to 10 equivalent weights, preferably 1.5 to 7 equivalent weights, more preferably 3 to 5 equivalent weight, per equivalent weight of the trialkoxysilane.

It is required to carry out the hydrolysis condensation of the trialkoxysilane under an acidic condition as described above, and an acid is generally used as a hydrolyzer for carrying out the hydrolysis under the above condition. Such an acid may be added to the trialkoxysilane or the colloidal silica beforehand, or may be added to a mixture thereof. Further, the acid may be added once or may be added twice or more times. The acid includes inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, nitrous acid, perchloric acid and sulfamic acid and organic acids such as formic acid, acetic acid, propionic acid, butyric acid, oxalic acid, succinic acid, maleic acid, lactic acid and p-toluenesulfonic acid. Organic carboxylic acids such as formic acid, acetic acid, propionic acid, lactic acid, oxalic acid, succinic acid and maleic acid are preferred since a pH can be easily controlled, and acetic acid is particularly preferred.

When the above acid is selected from the inorganic acids, an inorganic acid is generally used in a concentration of 0.0001 to 2 N, preferably 0.001 to 0.1 N. When it is selected from the organic acids, the amount of an organic acid per 100 parts by weight of the trialkoxysilane is in the range of from 0.1 to 50 parts by weight, preferably from 1 to 30 parts by weight.

Conditions under which the hydrolysis and condensation of the trialkoxysilane are carried out cannot be uniformly determined since they differ depending upon the kind of the trialkoxysilane and the kind and amount of the colloidal silica co-present in a reaction system. Generally, the temperature of the reaction system is 20 to 40°C, and the reaction time period is 1 hour to several days.

Process (2): (i) The tetraalkoxysilane of the above formula (II-2) is added to the reaction solution obtained by the reaction in the process (1), or (ii) the reaction solution obtained by the reaction in the process (1) and a reaction solution prepared in advance by hydrolysis condensation of the tetraalkoxysilane of the above formula (II-2) are mixed.

(i) When the tetraalkoxysilane is added to the reaction solution obtained by the reaction in the process (1) to carry out hydrolysis condensation, the hydrolysis condensation is carried out under an acidic condition. The reaction solution obtained by the reaction in the process (1) is generally acidic and contains water, so that the tetraalkoxysilane can be added as it is. Further, water and an acid may be added as required. The acid can be selected from the above-described acids, and a volatile acid such as acetic acid or hydrochloric acid is preferred. When the acid is selected from the inorganic acids, an inorganic acid is generally used in a concentration of 0.0001 to 2 N, preferably 0.001 to 0.1 N. When it is selected from the organic acids, the amount of an organic acid per 100 parts by weight of the tetraalkoxysilane is in the range of from 0.1 to 50 parts by weight, preferably from 1 to 30 parts by weight.

Water for the hydrolysis is used generally in an

amount of 1 to 100 equivalent weights, preferably 2 to 50 equivalent weights, more preferably 4 to 30 equivalent weight, per equivalent weight of the tetraalkoxysilane.

5 Conditions under which the hydrolysis and condensation of the tetraalkoxysilane are carried out cannot be uniformly determined since they differ depending upon the kind of the tetraalkoxysilane and the kind and amount of the colloidal silica co-present in a
10 reaction system. Generally, the temperature of the reaction system is 20 to 40°C, and the reaction time period is 10 minutes to several days.

 (ii) The reaction solution obtained by the reaction in the process (1) and a reaction solution prepared in
15 advance by hydrolysis condensation of the tetraalkoxysilane of the above formula (II-2) may be mixed. In this case, it is required to allow the tetraalkoxysilane to undergo hydrolysis and condensation beforehand. The above hydrolysis condensation is carried
20 out by a reaction under an acidic condition with water generally in an amount, per equivalent weight of the tetraalkoxysilane, of 1 to 100 equivalent weights, preferably 2 to 50 equivalent weights, more preferably 4 to 20 equivalent weights at 20 to 40°C for 1 hour to
25 several days. The above hydrolysis condensation uses an acid, and the acid is selected from the above acids. A volatile acid such as acetic acid or hydrochloric acid is preferred. When the acid is selected from the inorganic acids, an inorganic acid is generally used in
30 a concentration of 0.0001 to 2 N, preferably 0.001 to 0.1 N. When it is selected from the organic acids, the amount of an organic acid per 100 parts by weight of the tetraalkoxysilane is in the range of from 0.1 to 50 parts by weight, preferably from 1 to 30 parts by weight.

The mixing ratio of the components a to c that are the above organosiloxane resin solid component is determined in view of stability of an obtained coating composition solution and transparency, abrasion resistance, anti-scratch resistance, adhesion and cracking-occurrence of an obtained cured layer. Preferably, the component a is used in an amount of 15 to 35 % by weight, the component b is used in an amount of 55 to 75 % by weight as $R^2SiO_{3/2}$, and the component c is used in an amount of 3 to 20 % by weight as SiO_2 .

The amount ratio of the components a to c that constitute the organosiloxane resin solid component in the cured coating layer (II) is particularly preferably as follows: The amount of the component b as $R^2SiO_{3/2}$ is in the range of 60 to 75 % by weight, and (i) when the amount of the component b is at least 60 % by weight but less than 65 % by weight, the amount of the component a is 25 to 35 % by weight and the amount of the component c as SiO_2 is 3 to 10 % by weight. Alternatively, (ii) when the amount of the component b is at least 65 % by weight but not more than 75 % by weight, the amount of the component a is 15 to 30 % by weight and the amount of the component c as SiO_2 is 5 to 20 % by weight.

Generally, the above coating composition for the second layer preferably further contains a curing catalyst. The catalyst includes alkali metal salts such as lithium salts, sodium salts and potassium salts and quaternary ammonium salts such as benzyltrimethylammonium salt, tetramethylammonium salt and tetraethylammonium salt of aliphatic carboxylic acids such as formic acid, propionic acid, butyric acid, lactic acid, tartaric acid or succinic acid. Above all, sodium acetate, potassium acetate or benzyltrimethylammonium acetate is preferred. When a

dispersion of the colloidal silica in basic water is used as a colloidal silica and when an aliphatic carboxylic acid is used as an acid in the hydrolysis of the alkoxysilane, it means that a curing catalyst is

5 already contained in the coating composition. Although differing depending upon curing conditions, the content of the curing catalyst per 100 parts by weight of the organosiloxane resin solid component formed of the components a to c is preferably 0.01 to 10 parts by

10 weight, more preferably 0.1 to 5 parts by weight.

The solvent for the above coating solution for the second layer is required to stably dissolve the above organosiloxane resin solid component, and for this purpose, desirably, the solvent contains at least 20 %

15 by weight, preferably at least 50 % by weight, of an alcohol. Examples of the alcohol include methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-ethoxyethanol, 4-methyl-2-pentanol and 2-butoxyethanol. A low-boiling-point

20 alcohol having 1 to 4 carbon atoms is preferred, and 2-propanol is particularly preferred in view of solubility, stability and coating properties. The above solvent includes water which comes from the dispersion of the colloidal silica in water and does not contribute to the

25 hydrolysis, a lower alcohol formed together with the hydrolysis of the alkoxysilane, an organic solvent that comes from a dispersion of the colloidal silica in an organic solvent and an acid added for adjusting the pH of the coating composition. The acid used for the pH

30 adjustment includes inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, nitrous acid, perchloric acid and sulfamic acid and organic acids such as formic acid, acetic acid, propionic acid, butyric acid, oxalic acid, succinic acid,

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maleic acid, lactic acid and p-toluenesulfonic acid. Of these, an organic acid such as formic acid, acetic acid, propionic acid, butyric acid, oxalic acid, succinic acid or maleic acid is preferred in view of an easiness in pH control. Other solvent is required to be miscible with water/alcohol, and examples of the "other solvent" include ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone; ethers such as tetrahydrofuran, 1,4-dioxane and 1,2-dimethoxyethane; and esters such as ethyl acetate and ethoxyethyl acetate. The amount of the solvent per 100 parts by weight of the organosiloxane resin solid component formed of the components a to c is preferably 50 to 900 parts by weight, more preferably 150 to 700 parts by weight.

Desirably, the pH of the coating composition for the second layer is adjusted to 3.0 to 6.0, preferably 4.0 to 5.5 by adjusting the contents of the acid and the curing catalyst, whereby the gelation of the coating composition at room temperature can be prevented, so that the shelf life thereof can be increased. The coating composition can come to be a stabler composition when aged generally for several hours to several days.

The coating composition for the second layer is coated on the first coating layer formed on the transparent plastic substrate and cured under heat to form the second layer. The coating method can be selected from a bar coating method, a dip coating method, a flow coating method, a spray coating method, a spin coating method or a roller coating method as required depending upon the size and form of the substrate to be coated. In the substrate coated with the above composition, the solvent is dried and removed at a temperature between room temperature and the heat distortion temperature of the substrate, and then, the

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composition is cured under heat. The thermal curing is preferably carried out at a high temperature in a range in which no problem is caused on the heat resistance of the substrate, since the curing can be completed sooner.

5 At room temperature, the thermal curing does not proceed, and no cured coating layer can be obtained. This means that the organosiloxane resin solid component in the coating composition is a partial condensate. In the thermal curing process, residual Si-OH undergoes
10 condensation to form Si-O-Si bonds, and a coating layer having excellent abrasion resistance is formed. The thermal curing is preferably carried out in a range of from 50°C to 200°C for 10 minutes to 4 hours, more preferably in the range of from 80 to 160°C for 20
15 minutes to 3 hours. When the plastic forming the transparent plastic substrate is an aromatic polycarbonate resin, the thermal curing is carried out preferably in the range of from 100°C to 140°C for 30 minutes to 2 hours.

20 The thickness of the second layer is generally 2 to 10 μm , preferably 3 to 8 μm . When the thickness of the cured coating layer (II) is in the above range, there is no case where the cured coating layer (II) undergoes cracking due to a stress caused during its thermal
25 curing or where the adhesion between the cured coating layer (II) and the substrate decreases. The cured coating layer (II) having sufficient abrasion resistance, which is an object of the present invention, can be obtained.

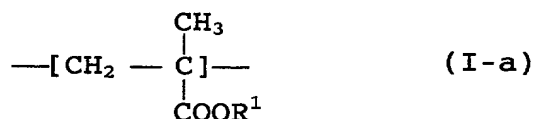
30 Further, The above coating compositions for the first layer and the second layer may contain a known leveling agent for improving coating properties and smoothness of the coating layers to be obtained. The amount thereof per 100 parts by weight of the coating

composition is preferably in the range of from 0.01 to 2 parts by weight. The above coating compositions may contain a dye, a pigment and a filler so long as the object of the present invention is not impaired.

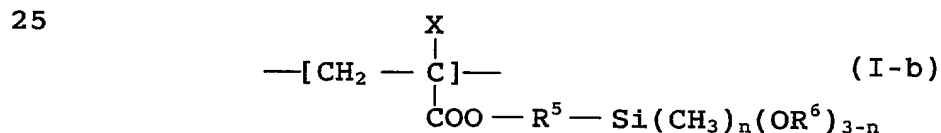
5 Particularly preferred embodiments of the transparent plastic composite material of the present invention will be explained below. That is, the transparent plastic composite material of the present invention having the transparent plastic substrate made
10 of an aromatic polycarbonate resin and any one of the following combinations (A) to (D) of the coating layer (I) and the cured coating layer (II) stacked on the surface thereof is the most preferred since they have excellent properties.

15 (A) A transparent plastic composite material wherein:

(1) the coating layer (I) is formed of a resin composition containing an acrylic copolymer resin which is formed of recurring units of the following formulae
20 (I-a) and (I-b),



wherein R^1 is as defined in the above formula (I-a),



wherein X, R^5 , R^6 and n are as defined in the above formula (I-b),

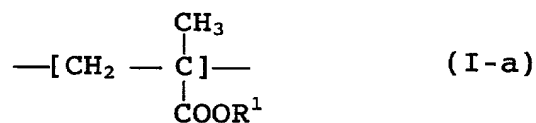
30 and which has a (I-a):(I-b) unit ratio in the range of from 97:3 to 70:30 and 3 to 60 parts by weight, per 100 parts by weight of the acrylic copolymer resin, of an ultraviolet absorbent, the ultraviolet absorbent having a solubility of 1.5 g/L or less in a solvent mixture

containing 100 parts by weight of isopropanol, 30 parts by weight of methanol and 15 parts by weight of water when measured at 25°C, and

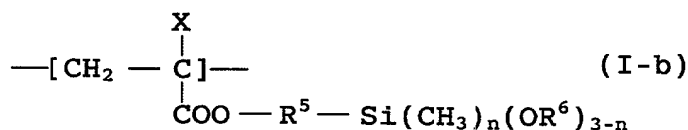
(2) the coating layer (II) is a thermally cured layer of a resin composition containing 15 to 35 % by weight of the component a, 55 to 75 % by weight, as $R^2SiO_{3/2}$, of the component b and 3 to 20 % by weight, as SiO_2 , of the component c.

(B) A transparent plastic composite material wherein:

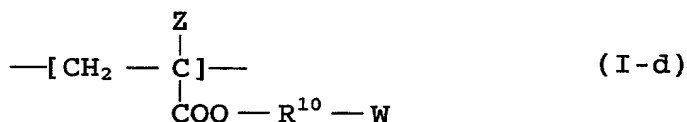
(1) the coating layer (I) is formed of a resin composition containing an acrylic copolymer resin which is formed of recurring units of the following formulae (I-a), (I-b) and (I-d),



wherein R^1 is as defined in the above formula (I-a),



wherein X , R^5 , R^6 and n are as defined in the above formula (I-b),



wherein Z , R^{10} and W are as defined in the above formula (I-d),

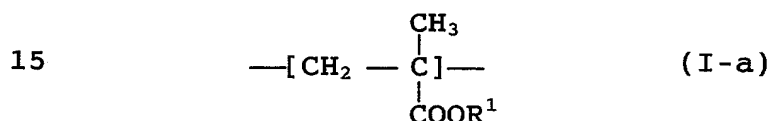
and which has a (I-a):(I-b):(I-d) unit ratio in the range of from 96.7-60:3-30:0.3-15 and 3 to 60 parts by weight, per 100 parts by weight of the acrylic copolymer resin, of an ultraviolet absorbent, the ultraviolet absorbent having a solubility of 1.5 g/L or less in a solvent mixture containing 100 parts by weight of

isopropanol, 30 parts by weight of methanol and 15 parts by weight of water when measured at 25°C, and

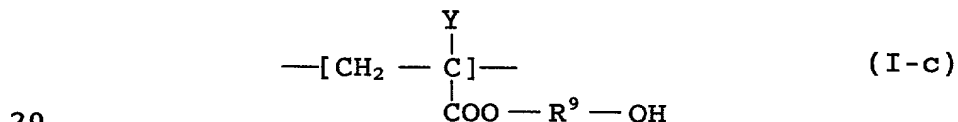
(2) the coating layer (II) is a thermally cured layer of a resin composition containing 15 to 35 % by weight of the component a, 55 to 75 % by weight, as $R^2SiO_{3/2}$, of the component b and 3 to 20 % by weight, as SiO_2 , of the component c.

(C) A transparent plastic composite material wherein:

(1) the coating layer (I) is formed of a resin composition containing 100 parts by weight of an acrylic copolymer resin which is formed of recurring units of the following formulae (I-a) and (I-c),



wherein R^1 is as defined in the above formula (I-a),



wherein Y and R^9 are as defined in the above formula (I-c)

and which has a (I-a):(I-c) unit ratio in the range of from 95:5 to 60:40, a mixture (as $R^7_xSiO_{4-x/2}$) of hydrolysis condensates of a compound of the formula (I-e),



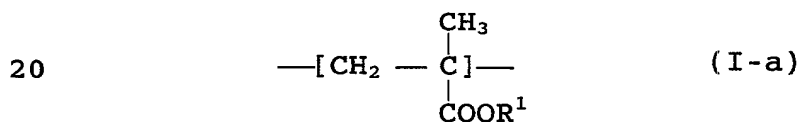
wherein R^7 , R^8 and x are as defined in the above formula (I-e), the mixture having such an amount that the ratio of the acrylic copolymer resin:the hydrolysis condensates comes to be 99:1 to 60:40 by weight, a melamine resin in such an amount that the amount thereof per 100 parts by weight of the total of the acrylic copolymer resin and the hydrolysis condensates comes to

be 3 to 15 parts by weight, and 3 to 60 parts by weight, per 100 parts by weight of the acrylic copolymer resin, of an ultraviolet absorbent, the ultraviolet absorbent having a solubility of 1.5 g/L or less in a solvent mixture containing 100 parts by weight of isopropanol, 30 parts by weight of methanol and 15 parts by weight of water when measured at 25°C, and

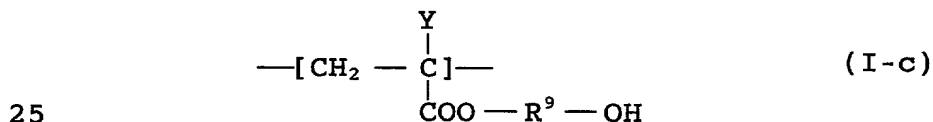
(2) the coating layer (II) is a thermally cured layer of a resin composition containing 15 to 35 % by weight of the component a, 55 to 75 % by weight, as $R^2SiO_{3/2}$, of the component b and 3 to 20 % by weight, as SiO_2 , of the component c.

(D) A transparent plastic composite material wherein:

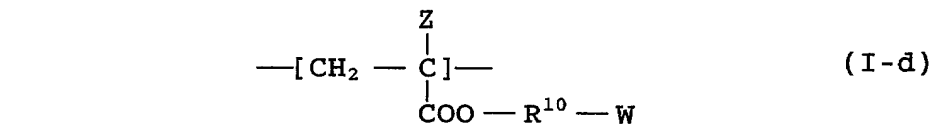
(1) the coating layer (I) is formed of a resin composition containing 100 parts by weight of an acrylic copolymer resin which is formed of recurring units of the following formulae (I-a), (I-c) and (I-d),



wherein R^1 is as defined in the above formula (I-a),



wherein Y and R^9 are as defined in the above formula (I-c),



wherein Z, R^{10} and W are as defined in the above formula (I-d),

and which has a (I-a):(I-c):(I-d) unit ratio in the range of from 94.7-50:5-40:0.3-15, a mixture (as $R^7_rSiO_4$ -

$r/2$) of hydrolysis condensates of a compound of the formula (I-e),



wherein R^7 , R^8 and r are as defined in the above
 5 formula (I-e), the mixture having such an amount that the ratio of the acrylic copolymer resin:the hydrolysis condensates comes to be 99:1 to 60:40 by weight, a melamine resin in such an amount that the amount thereof per 100 parts by weight of the total of the acrylic
 10 copolymer resin and the hydrolysis condensates comes to be 3 to 15 parts by weight, and 3 to 60 parts by weight, per 100 parts by weight of the acrylic copolymer resin, of an ultraviolet absorbent, the ultraviolet absorbent having a solubility of 1.5 g/L or less in a solvent
 15 mixture containing 100 parts by weight of isopropanol, 30 parts by weight of methanol and 15 parts by weight of water when measured at 25°C, and

(2) the coating layer (II) is a thermally cured layer of a resin composition containing 15 to 35 % by
 20 weight of the component a, 55 to 75 % by weight, as $R^2SiO_{3/2}$, of the component b and 3 to 20 % by weight, as SiO_2 , of the component c.

The thus-obtained surface-protected transparent plastic composite material of the present invention has
 25 a first layer formed mainly of the acrylic resin and a second layer formed by thermally curing the organosiloxane resin made from colloidal silica, the trialkoxysilane hydrolysis condensate and the tetraalkoxysilane hydrolysis condensate, so that it
 30 constitutes a composite material having unconventionally high-level abrasion resistance.

The transparent plastic composite material of the present invention has a thickness in the range of from 0.001 to 10 mm, preferably 0.02 to 8 mm. When the

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plastic constituting the transparent plastic substrate is an aromatic polycarbonate resin in particular, practically, the above thickness is preferably in the range of from 0.1 to 8 mm. Further, the transparent plastic composite material of the present invention undergoes no cracking under high-temperature and high-humidity conditions, and after it is maintained in boiling water for 3 hours, the occurrence of cracking is substantially not observed on the surface thereof.

The above transparent plastic composite material can be suitably used in windows of an aircraft, a car and an automobile, windows of a building, a house, a garage, a green room and an arcade, a headlight lens, an optical lens, a mirror, eyeglasses, goggles, an insulating wall, a lens of a traffic light lamp, a curved mirror, a windshield, a windscreen, a name plate, other various sheets, films, and the like.

When subjected to a 1,000-rotation Taber abrasion test (ASTM D1044) using a CS-10F abrasion wheel supplied by Calibrase under a load of 500 g, the transparent plastic composite material obtained in the present invention shows a change of 2 % or less between its haze values before and after the test. That is, the transparent plastic composite material obtained in the present invention satisfies the JIS standard requiring that the outer side of windshield of an automobile should satisfy a change of 2 % or less between its haze values before and after the test with a Taber abrasion tester under conditions similar to the above, and such a composite material can be suitably used as a window glass of an automobile and an aircraft.

Examples

The present invention will be explained more in

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detail with reference to Examples hereinafter, while the present invention shall not be limited by Examples.

Polycarbonate resin composite materials obtained were evaluated by the following methods. In Examples, "part" and "%" stand for "part by weight" and "% by weight".

(1) Evaluation of appearance: The appearance of a coating layer of a test piece was visually observed (for a foreign matter) and for a cracking.

(2) Adhesion: A coating layer was cut at intervals of 1 mm with a cutter to make 100 sections, an adhesive tape (trade name "Cellotape"®) supplied by Nichiban was attached under pressure and intensely peeled off in the perpendicular direction, and the adhesion was evaluated on the basis of the number of sections remaining on a substrate (according to JIS K5400).

Further, the procedure of attaching and peeling a tape to/from the sections was further repeated twice, and the adhesion was evaluated on the basis of sections remaining on the substrate.

(3) Abrasion resistance: A 1,000-rotation Taber abrasion test (ASTM D1044) was carried out using a CS-10F abrasion wheel supplied by Calibrase under a load of 500 g, and a difference ΔH (%) between a haze (%) before the Taber abrasion test and a haze (%) after the Taber abrasion test was determined for evaluation (according to ASTM D1044).

(Haze = $T_d/T_t \times 100$, T_d : transmissivity of scattered light, T_t : transmissivity of total light)

(Haze measurement was conducted with a haze meter 1001DP supplied by Nippon Denshoku K.K.)

(4) Durability against boiling water: A test piece was immersed in boiling water for 3 hours, and then it was evaluated for an appearance and adhesion.

(5) Weatherability: A test piece was subjected to an

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5 appearance, adhesion and a change (ΔYI) between
yellowing indexes before and after the test. (Yellowing
index (YI) was measured with a spectral color tester SE-
2000 supplied by Nippon Denshoku K.K.)

(Synthesis of acrylic resins (AC-1) - (AC-16))

15 A flask having a reflux condenser and a stirrer and
having nitrogen substituted for air inside was charged
with 65 parts of methyl methacrylate (to be abbreviated
as "MMA" hereinafter), 25 parts of 2-(2'-hydroxy-5'-
methacryloxyethylphenyl)benzotriazole (to be abbreviated
20 as "MEBT" hereinafter), 10 parts of 3-
methacryloxypropyl-trimethoxysilane (to be abbreviated
as "MPTMS" hereinafter), 0.16 part of
azobisisobutyronitrile and 200 parts of 1,2-
dimethoxyethane, and these contents were mixed and
25 dissolved. Then, the mixture was allowed to react under
nitrogen current at 70°C for 6 hours. The resultant
reaction mixture was added to n-hexane for re-
precipitation and purification, to give 86 parts of an
acrylic copolymer resin (to be abbreviated as "AC-1"
30 hereinafter) having an MMA/MEBT/MPTMS composition ratio
of 65/25/10 by weight ratio (85/10/5 by molar ratio).
The above copolymer had a weight average molecular
weight of 90,000.

Referential Examples 2 - 16

Synthesis was carried out in the same manner as in Referential Example 1 except that the monomer composition was changed as shown in Table 1, to give acrylic resins (AC-2 to AC-16). Table 1 shows compositions and molecular weights of the acrylic resins.

Table 1

Acrylic resin	Monomer composition						Molecular weight
	MMA	EMA	MEBT	MEBP	HEMA	MPTMS	
(AC-1)	65		25			10	90,000
(AC-2)	72		13			15	140,000
(AC-3)	60		13		27		70,000
(AC-4)	74		15		11		80,000
(AC-5)	64		25		11		60,000
(AC-6)	77		13			10	90,000
(AC-7)	60	15		14	11		80,000
(AC-8)	60	15	14		11		100,000
(AC-9)	70				39		80,000
(AC-10)	90.1				13		180,000
(AC-11)	95.1					12.4	120,000
(AC-12)		80			10	10	140,000
(AC-13)	90.1					24.8	150,000
(AC-14)	70	15	10		5		100,000
(AC-15)	36					64	80,000
(AC-16)	30		30		30	10	60,000

10 (Preparation of organosiloxane resin solution)

Referential Example 17

142 Parts of methyltrimethoxysilane, 72 parts of distilled water and 20 parts of acetic acid were mixed with cooling with ice water. The mixture was stirred at 25°C for 1 hour and diluted with 116 parts of isopropanol, to give 350 parts of a methyltrimethoxysilane hydrolysis condensate solution (to be abbreviated as "X" hereinafter).

Referential Example 18

20 208 Parts of tetraethoxysilane and 81 parts of 0.01 N hydrochloric acid were mixed with cooling with ice

5 (Preparation of acrylic resin solutions (h-1) - (h-21))
Referential Example 19

Referential Example 20 - 39

Acrylic resin solutions (h-2) to (h-21) were prepared from various acrylic copolymer resins in the same manner as in Referential Example 19. Table 2 shows compositions thereof.

Table 2

Acrylic resin solution	Acrylic resin		MEK	MTBK	2-BuOH	IPA	EtOH	EGE	PMA
	Type No.	Amount							
(h-1)	(AC-1)	9		60	30				
(h-2)	(AC-2)	18		60	20				
(h-3)	(AC-3)	14	15.7	31.2	10				13.4
(h-4)	(AC-4)	13	16.3	27	11			9.6	
(h-5)	(AC-5)	15		36		10			18
(h-6)	(AC-5)	10.5	15	30	11.5			20	
(h-7)	(AC-6)	16	16	40	28				
(h-8)	(AC-7)	15	5	30	18				11
(h-9)	(AC-8)	10.5	10	40	10			12.9	
(h-10)	(AC-9)	6	18	36	25	5			
(h-11)	(AC-10)	6.7	18	36	25	4.9			
(h-12)	(AC-11)	18		54	26				
(h-13)	(AC-5)	15	4.9	28	21				10
(h-14)	(AC-12)	9		60	30				
(h-15)	(AC-11)	20		60	20				
(h-16)	(AC-13)	10		60	20			10	
(h-17)	(AC-9)	7.4	37	18.5		12.9	4.9	9.2	
(h-18)	(AC-9)	11.5	43.2		9.3			21.6	
(h-19)	(AC-14)	15	20	20	14				14
(h-20)	(AC-15)	9		60	30				
(h-21)	(AC-16)	10		45	20				25

(Preparation of organosiloxane resin solutions (i-1) - (i-5)

Referential Example 40

80 Parts of the methyltrimethoxysilane hydrolysis condensate solution (X), 20 parts of the tetraethoxysilane hydrolysis condensate solution (Y) and 1 part of tetrabutylammonium hydroxide as a curing catalyst were mixed to give an organosiloxane resin solution (i-1).

Referential Examples 41 - 44

Organosiloxane resin solutions (i-2) to (i-5) having respective compositions were prepared in the same manner as in Referential Example 40. Table 3 shows the respective compositions.

Table 3

Organosiloxane resin solution	X	Y	AcONa	Nbu ₄ OH
i-1	80	20		1
i-2	100		0.5	
i-3	100			1
i-4	100			
i-5	70	30		0.8

(Preparation of Melamine resin formulations (j-1) - (j-4)

Referential Example 45

100 Parts of Cymel 303 (hexamethoxymethylated melamine resin supplied by Mitsui-Cytec) and 3 parts of p-toluenesulfonic acid as a curing catalyst were mixed to give a melamine resin formulation (j-1).

Referential Examples 46 - 48

Melamine resin formulations (j-2) to (j-4) having respective compositions were prepared in the same manner as in Referential Example 45. Table 4 shows the

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manner as in Referential Example 49 or 51. Table 5 shows the respective compositions.

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TABLE 5

Table 5

First layer coating solution	Acrylic resin solution		Organosiloxane resin solution		Melamine resin formulation		Ultraviolet absorbent		Total amount (part)
	Type	Amount (part)	Type	Amount (part)	Type	Amount (part)	Type	Amount (part)	
(I-1)	(h-1)	99.0					UV-1	1.0	100.0
(I-2)	(h-2)	98.0					UV-2	2.0	100.0
(I-3)	(h-3)	84.3	(i-1)	12	j-1	1.7	UV-3	2.0	100.0
(I-4)	(h-4)	76.9	(i-2)	20	j-3	1.1	UV-1	2.0	100.0
(I-5)	(h-5)	79.0	(i-3)	20			UV-1	1.0	100.0
(I-6)	(h-6)	87.0	(i-2)	10.5	j-4	1	UV-1	1.5	100.0
(I-7)	(h-7)	100.0							100.0
(I-8)	(h-8)	79.0	(i-5)	20	j-1	1			100.0
(I-9)	(h-9)	83.4	(i-2)	15	j-1	1.6			100.0
(I-10)	(h-10)	90.0	(i-3)	7.5	j-1	1	UV-1	1.5	100.0
(I-11)	(h-11)	90.6	(i-2)	7.5	j-1	0.9	UV-1	1.0	100.0
(I-12)	(h-12)	98.0					UV-1	2.0	100.0
(I-13)	(h-13)	78.9	(i-2)	20	j-1	1.1			100.0
(I-14)	(h-14)	99.0					UV-4	1.0	100.0
(I-15)	(h-15)	100.0							100.0
(I-16)	(h-16)	100.0							100.0
(I-17)	(h-17)	89.9	(i-1)	9.2	j-1	0.9			100.0
(I-18)	(h-17)	89.9	(i-4)	9.2	j-2	0.9			100.0
(I-19)	(h-18)	85.6	(i-4)	14.4					100.0
(I-20)	(h-19)	83.0	(i-2)	15	j-1	2			100.0
(I-21)	(h-19)	83.0	(i-2)	15	j-1	1	UV-1	1.0	100.0
(I-22)	(h-20)	99.0	(i-2)				UV-1	1.0	100.0
(I-23)	(h-21)	100.0							100.0

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12 Parts of distilled water and 20 parts of acetic acid were added to 100 parts of a water-dispersible

colloidal silica dispersion (S-30), and the mixture was stirred. 130 Parts of methyltrimethoxysilane was added to the resultant dispersion with cooling in an ice water bath. The mixture was stirred at 25°C for 1 hour, and 5 15.2 parts of tetramethoxysilane was added to the resultant reaction mixture. The mixture was stirred at 25°C for 1 hour, then, 1 part of sodium acetate as a curing catalyst was mixed therewith at room temperature, and the mixture was diluted with 200 parts of 10 isopropanol to give 478.2 parts of a second layer coating solution (II-3). The coating solution had a pH of 4.8.

Referential Examples 75 - 85

Second layer coating solutions (II-4) to (II-14) 15 having compositions shown in Table 6 were prepared in the same manner as in Referential Example 72 or 74. Table 6 shows the respective compositions.

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Table 6

Second layer coating solution	S-30	MTMOS	Y	TMOS	Acetic acid	Water	AcONa	AcOK	Nbu ₄ OH	IPA	pH of coating solution
(II-1)	100	130	30		20	2	2			200	5.0
(II-2)	100	122	50		20			1		408	4.7
(II-3)	100	130		15.2	20	12	1			200	4.8
(II-4)	100	151.1	33.3		11.1	10		2.2		188.9	5.4
(II-5)	100	134		10.1	20	20	1			200	4.7
(II-6)	100	236.8	100		50	60			3	50	4.8
(II-7)	100	139.2	42.8		40	10	2			100	4.7
(II-8)	100	86.8	11.2		10				2	150	5.3
(II-9)	100	260.5	41.7		60	60	4			50	4.9
(II-10)	100	134	20		20	12	1			200	4.8
(II-11)	100	142			20	2	2			236	4.9
(II-12)		146		71	20	90	2			173	4.8
(II-13)	100	54.8	15		10		2			200	5.4
(II-14)	100	137	262.5		20		1			200	4.7

Table 6 (continued)

Second layer Composition	Colloidal silica	Weight ratio	
		Trialkoxysilane (as $R^2SiO_{3/2}$)	Tetraalkoxysilane (as SiO_2)
(II-1)	30	64	6
(II-2)	30	60	10
(II-3)	30	64	6
(II-4)	27	67	6
(II-5)	30	66	4
(II-6)	18	70	12
(II-7)	28	64	8
(II-8)	40	57	3
(II-9)	18	77	5
(II-10)	30	66	4
(II-11)	30	70	
(II-12)		72	28
(II-13)	50	45	5
(II-14)	20	45	35

Example 1

The first layer coating solution (I-1) was applied onto a 0.5 mm thick transparent sheet made of a polycarbonate resin (to be abbreviated as "PC resin" hereinafter) with a wire bar (bar coating method), and the applied coating solution was left at 25°C for 20 minutes and then thermally cured at 120°C for 20 minutes. The first layer had a thickness of 2.0 μm . Then, the second layer coating solution (II-1) was applied onto the coating surface of the sheet with a wire bar, and the applied coating solution was left at 25°C for 20 minutes and then thermally cured at 120°C for 1 hour. The second layer had a thickness of 5.0 μm . Table 7 shows results of evaluation of the resultant PC resin composite material.

Example 2

A 0.5 mm thick transparent sheet made of a PC resin was vertically suspended, and the first layer coating solution (I-2) was applied by flowing it from an upper portion of the sheet with a nozzle. The applied coating solution was left at 25°C for 20 minutes and then thermally cured at 120°C for 30 minutes. The first layer had a thickness of 3.0 μm . Then, the second layer coating solution (II-2) was applied on the coating surface of the sheet in the same manner as in the formation of the first layer, and the applied coating solution was left at 25°C for 20 minutes and then thermally cured at 120°C for 2 hours. The second layer had a thickness of 3.5 μm . Table 7 shows results of evaluation of the resultant PC resin composite material.

Example 3

A dip coating vessel having the form of a rectangular parallelepiped was filled with the first layer coating solution (I-3), and a 0.5 mm thick

transparent sheet made of a PC resin was pre-dipped in the coating solution, lifted up at a constant rate and left at 25°C for 30 minutes, followed by thermal curing at 120°C for 40 minutes. The first layer had a thickness of 4.0 μm . Then, the second layer coating solution (II-3) was applied onto the coating surface of the sheet in the same manner as in the formation of the first layer, and the applied coating solution was left at 25°C for 20 minutes and then thermally cured at 110°C for 2 hours.

- 5
- 10 The second layer had a thickness of 6.0 μm . Table 7 shows results of evaluation of the resultant PC resin composite material.

Examples 4 - 24 and Comparative Examples 1 - 5

- 15 PC resin composite materials were prepared by carrying out application and thermally curing treatments in the same manner as in Example 3. The PC resin composite materials were evaluated for performances, and Table 7 shows the results.

Table 7

	First layer coating solution	Thickness of first layer (μm)	Second layer coating solution	Thickness of second layer (μm)	Appearance	Initial haze	Abrasion resistance
Ex.1	(I-1)	2.0	(II-1)	5.0	Excellent	0.1	1.8
Ex.2	(I-2)	3.0	(II-2)	3.5	Excellent	0.1	1.6
Ex.3	(I-3)	4.0	(II-3)	6.0	Excellent	0.1	1.8
Ex.4	(I-4)	3.5	(II-4)	4.0	Excellent	0.1	1.8
Ex.5	(I-5)	3.0	(II-5)	6.0	Excellent	0.1	1.9
Ex.6	(I-6)	2.0	(II-6)	5.0	Excellent	0.1	1.9
Ex.7	(I-7)	5.0	(II-7)	4.0	Excellent	0.1	1.7
Ex.8	(I-8)	6.0	(II-1)	5.0	Excellent	0.2	1.8
Ex.9	(I-9)	5.0	(II-1)	4.0	Excellent	0.1	1.8
Ex.10	(I-10)	5.0	(II-1)	4.0	Excellent	0.1	1.8
Ex.11	(I-11)	5.0	(II-1)	5.0	Excellent	0.1	1.8
Ex.12	(I-12)	5.0	(II-1)	4.0	Excellent	0.1	1.8
Ex.13	(I-1)	2.0	(II-1)	5.0	Excellent	0.1	2.1
Ex.14	(I-5)	3.0	(II-8)	4.0	Excellent	0.1	2.1
Ex.15	(I-13)	4.0	(II-8)	4.0	Excellent	0.1	2.1
Ex.16	(I-14)	4.0	(II-9)	5.0	Excellent	0.1	1.8
Ex.17	(I-15)	2.5	(II-1)	5.0	Excellent	0.1	1.8
Ex.18	(I-16)	3.0	(II-2)	3.5	Excellent	0.1	1.6
Ex.19	(I-17)	2.5	(II-10)	5.0	Excellent	0.1	1.9
Ex.20	(I-18)	2.5	(II-10)	5.0	Excellent	0.1	1.9
Ex.21	(I-20)	3.0	(II-1)	5.0	Excellent	0.1	1.8
Ex.22	(I-21)	3.0	(II-1)	5.0	Excellent	0.1	1.8
Ex.23	(I-22)	3.0	(II-1)	5.0	Excellent	0.1	1.8
Ex.24	(I-19)	4.0	(II-4)	7.0	Excellent	0.3	1.8

Ex.: Example

Table 7 (continued)

	Adhesion		Boiling water immersion test		Weatherability test				
	First time	Third time	Appearance	Adhesion		Appearance	Adhesion		ΔYI
				First time	Third time		First time	Third time	
Ex.1	100	100	Excellent			Excellent	100	100	0.2
Ex.2	100	100	Excellent	100	100	Excellent	100	100	0.3
Ex.3	100	100	Excellent	100	100	Excellent	100	100	0.2
Ex.4	100	100	Excellent	100	100	Excellent	100	100	0.3
Ex.5	100	100	Excellent	100	100	Excellent	100	100	0.2
Ex.6	100	100	Excellent	100	100	Excellent	100	100	0.3
Ex.7	100	100	Excellent	100	100	Excellent	100	100	0.2
Ex.8	100	100	Excellent	100	100	Excellent	100	100	0.3
Ex.9	100	100	Excellent	100	100	Excellent	100	100	0.4
Ex.10	100	100	Excellent	100	100	Excellent	100	100	0.3
Ex.11	100	100	Excellent	100	100	Excellent	100	100	0.3
Ex.12	100	100	Excellent	100	100	Excellent	100	100	0.1
Ex.13	100	100	Excellent	100	100	Excellent	100	100	0.3
Ex.14	100	100	Excellent	100	50	Excellent	100	100	0.2
Ex.15	100	100	Excellent	100	100	Excellent	100	100	0.3
Ex.16	100	100	Excellent	100	100	Yellowing	100	100	3.8
Ex.17	100	100	Excellent	100	100	Yellowing	100	50	16.8
Ex.18	100	100	Excellent	100	100	Yellowing	100	20	17.5
Ex.19	100	100	Excellent	100	80	Yellowing	100	100	18.5
Ex.20	100	100	Excellent	100	100	Yellowing	100	80	19.6
Ex.21	100	100	Excellent	100	80	Excellent	100	100	0.5
Ex.22	100	100	Excellent	100	20	Excellent	100	100	0.2
Ex.23	100	100	Excellent	100	20	Excellent	100	100	0.3
Ex.24	100	100	Excellent	100	80	Yellowing	100	50	20.8

Ex.: Example

Table 7 (continued)

	First layer coating solution	Thickness of first layer (μm)	Second layer coating solution	Thickness of second layer (μm)	Appearance	Initial haze	Abrasion resistance
C.Ex.1	(I-18)	3.0	(II-11)	5.0	Excellent	0.1	2.9
C.Ex.2	(I-18)	3.0	(II-12)	5.0	Excellent	0.1	4.7
C.Ex.3	(I-18)	3.0	(II-13)	3.5	Excellent	0.3	2.5
C.Ex.4	(I-18)	3.0	(II-14)	3.5	Cracking		
C.Ex.5	(I-23)	3.0	(II-1)	5.0	Excellent	0.2	

	Adhesion		Boiling water immersion test		Weatherability test			
	First time	Third time	Appearance	Adhesion	Appearance		Adhesion	ΔYI
				First time	Third time		First time	Third time
C.Ex.1	100	100	Excellent	100	100	Yellowing	100	50
C.Ex.2	100	100	Excellent	100	100	Yellowing	100	20
C.Ex.3	100	100	Cracking			Yellowing	100	0
C.Ex.4								
C.Ex.5	20	0	Excellent	0		Peeling of layer		

C.Ex.: Comparative Example

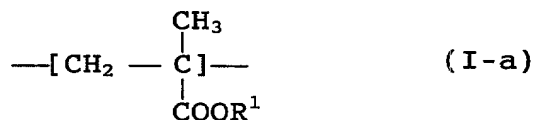
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CLAIMS

1. A surface-protected plastic composite material comprising a transparent plastic, a coating layer (I) as
 5 a first layer stacked on the transparent plastic substrate and a thermally cured coating layer (II) as a second layer stacked on the first layer, the coating layer (I) being formed of a resin composition containing at least 50 % by weight, based on the resin content
 10 thereof, of an acrylic resin which is an acrylic resin containing at least 50 mol% of recurring unit of the following formula (I-a),



15

wherein R^1 is an alkyl group having 1 to 4 carbon atoms,

the thermally cured coating layer (II) being made of an organosiloxane resin formed from the following
 20 components a, b and c,

(A) colloidal silica (component a),

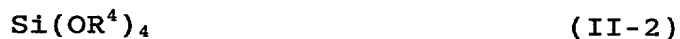
(B) a hydrolysis condensate (component b) of a trialkoxysilane of the following formula (II-1),



25

wherein R^2 is an alkyl group having 1 to 4 carbon atoms, a vinyl group or an alkyl group which has 1 to 3 carbon atoms and is substituted with at least one group selected from the group consisting of methacryloxy, amino, glycidoxy and 3,4-epoxycyclohexyl and R^3 is an
 30 alkyl group having 1 to 4 carbon atoms, and

(C) a hydrolysis condensate (component c) of a tetraalkoxysilane of the following formula (II-2),



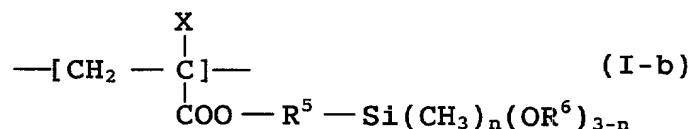
wherein R^4 is an alkyl group having 1 to 4 carbon

atoms, the organosiloxane resin containing 5 to 45 % by weight of the component a, 50 to 80 % by weight, as $R^2SiO_{3/2}$, of the component b and 2 to 30 % by weight, as SiO_2 , of the component c.

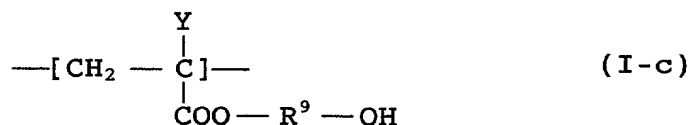
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2. The transparent plastic composite material of claim 1, wherein the acrylic resin of the coating layer (I) is an acrylic copolymer resin having recurring units of the said formula (I-a) and the following formula (I-b)

10 and/or the following formula (I-c),



in which X is a hydrogen atom or methyl, R^5 is an alkylene group having 2 to 5 carbon atoms, R^6 is an alkyl group having 1 to 4 carbon atoms and n is an integer of 0 or 1,

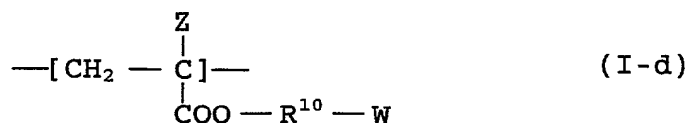


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in which Y is a hydrogen atom or methyl and R^9 is an alkylene group having 2 to 5 carbon atoms,

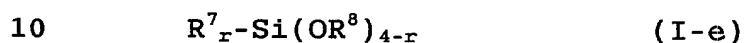
and further wherein the acrylic copolymer resin has a (I-a):[(I-b) + (I-c)] molar ratio of the units in the range of from 99.5:0.5 to 50:50.

3. The transparent plastic composite material of claim 2, wherein the acrylic copolymer resin is an acrylic copolymer resin containing 0.3 to 40 mol%, based on the total units of the above formulae (I-a) and [(I-b) + (I-c)], of units of the following formula (I-d),



wherein Z is a hydrogen atom or methyl, R^{10} is an alkylene group having 2 to 5 carbon atoms and W is an ultraviolet absorbent residue.

- 5 4. The transparent plastic composite material of any one of claims 1 to 3, wherein the coating layer (I) is formed of a mixture of the acrylic resin with a hydrolysis condensate of a compound of the following formula (I-e),



- wherein R^7 is an alkyl group having 1 to 4 carbon atoms, a vinyl group or an alkyl group which is substituted with one or more groups selected from the class consisting of methacryloxy, amino, glycidoxy and
 15 3,4-epoxycyclohexyl and has 1 to 3 carbon atoms, R^8 is an alkyl group having 1 to 4 carbon atoms, and r is an integer of 0 to 2, the mixture having an acrylic resin:hydrolysis condensate (as $R^7_r-SiO_{4-r/2}$) amount ratio by weight in the range of from 99:1 to 60:40,

20

5. The transparent plastic composite material of claim 4, wherein the coating layer (I) further contains a melamine resin in the range of from 1 to 20 parts by weight per 100 parts by weight of the total of the
 25 acrylic resin and the hydrolysis condensate of the compound of the formula (I-e).

6. The transparent plastic composite material of any one of claims 1 to 4, wherein the coating layer (I)
 30 further contains 0.7 to 100 parts by weight, per 100 parts by weight of the acrylic resin, of an ultraviolet absorbent.

7. The transparent plastic composite material of claim

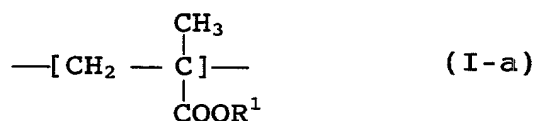
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6, wherein the ultraviolet absorbent has a solubility of 1.5 g/L or less in a solvent mixture containing 100 parts by weight of isopropanol, 30 parts by weight of methanol and 15 parts by weight of water when measured at 25° C.

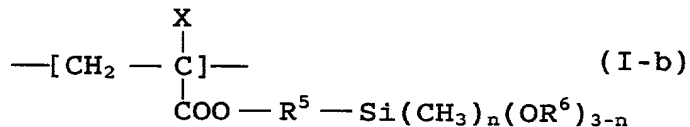
8. The transparent plastic composite material of claim 1, wherein the coating layer (II) is a thermally cured layer of a resin composition containing 15 to 35 % by weight of the component a, 55 to 75 % by weight, as $R^2SiO_{3/2}$, of the component b and 3 to 20 % by weight, as SiO_2 , of the component c.

9. The transparent plastic composite material of claim 1, wherein:

(1) the coating layer (I) is formed of a resin composition containing an acrylic copolymer resin which is formed of recurring units of the following formulae (I-a) and (I-b),



wherein R^1 is as defined in the foregoing formula (I-a),



wherein X, R^5 , R^6 and n are as defined in the foregoing formula (I-b),

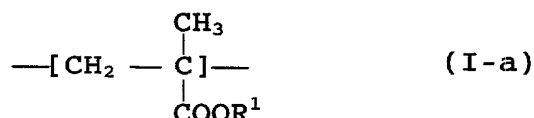
and which has a (I-a):(I-b) unit ratio in the range of from 97:3 to 70:30 and 3 to 60 parts by weight, per 100 parts by weight of the acrylic copolymer resin, of an ultraviolet absorbent, the ultraviolet absorbent having a solubility of 1.5 g/L or less in a solvent mixture

containing 100 parts by weight of isopropanol, 30 parts by weight of methanol and 15 parts by weight of water when measured at 25°C, and

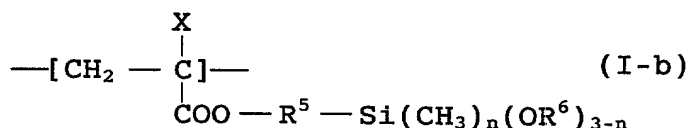
(2) the coating layer (II) is a thermally cured layer of a resin composition containing 15 to 35 % by weight of the component a, 55 to 75 % by weight, as $R^2SiO_{3/2}$, of the component b and 3 to 20 % by weight, as SiO_2 , of the component c.

10 10. The transparent plastic composite material of claim 1, wherein:

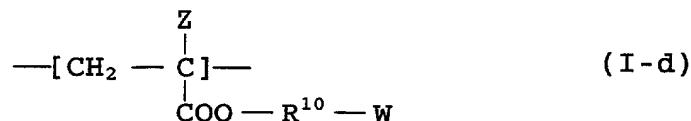
(1) the coating layer (I) is formed of a resin composition containing an acrylic copolymer resin which is formed of recurring units of the following formulae (I-a), (I-b) and (I-d),



wherein R^1 is as defined in the foregoing formula (I-a),



wherein X, R^5 , R^6 and n are as defined in the foregoing formula (I-b),



wherein Z, R^{10} and W are as defined in the foregoing formula (I-d),

and which has a (I-a):(I-b):(I-d) unit ratio in the range of from 96.7-60:3-30:0.3-15 and 3 to 60 parts by weight, per 100 parts by weight of the acrylic copolymer resin, of an ultraviolet absorbent, the ultraviolet

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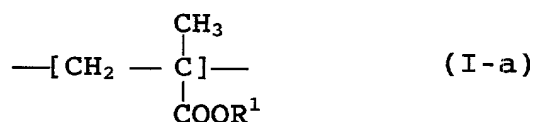
absorbent having a solubility of 1.5 g/L or less in a solvent mixture containing 100 parts by weight of isopropanol, 30 parts by weight of methanol and 15 parts by weight of water when measured at 25°C, and

- 5 (2) the coating layer (II) is a thermally cured layer of a resin composition containing 15 to 35 % by weight of the component a, 55 to 75 % by weight, as $R^2SiO_{3/2}$, of the component b and 3 to 20 % by weight, as SiO_2 , of the component c.

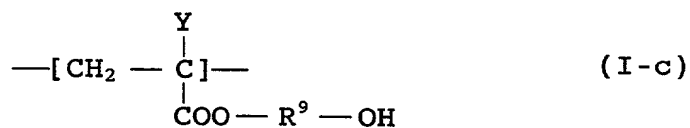
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11. The transparent plastic composite material of claim 1, wherein:

- 15 (1) the coating layer (I) is formed of a resin composition containing 100 parts by weight of an acrylic copolymer resin which is formed of recurring units of the following formulae (I-a) and (I-c),



- 20 wherein R^1 is as defined in the foregoing formula (I-a),



- 25 wherein Y and R^9 are as defined in the foregoing formula (I-c),
and which has a (I-a):(I-c) unit ratio in the range of from 95:5 to 60:40, a mixture (as $R^7_rSiO_{4-r/2}$) of hydrolysis condensates of a compound of the formula (I-e),
30 e),



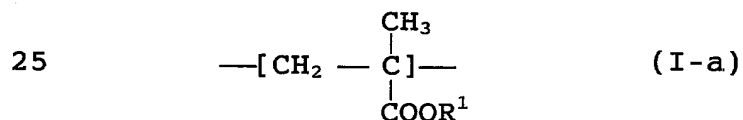
wherein R^7 , R^8 and r are as defined in the foregoing formula (I-e), the mixture having such an amount that the ratio of the acrylic copolymer resin:the hydrolysis

condensates comes to be 99:1 to 60:40 by weight, a melamine resin in such an amount that the amount thereof per 100 parts by weight of the total of the acrylic copolymer resin and the hydrolysis condensates comes to be 3 to 15 parts by weight, and 3 to 60 parts by weight, per 100 parts by weight of the acrylic copolymer resin, of an ultraviolet absorbent, the ultraviolet absorbent having a solubility of 1.5 g/L or less in a solvent mixture containing 100 parts by weight of isopropanol, 30 parts by weight of methanol and 15 parts by weight of water when measured at 25°C, and

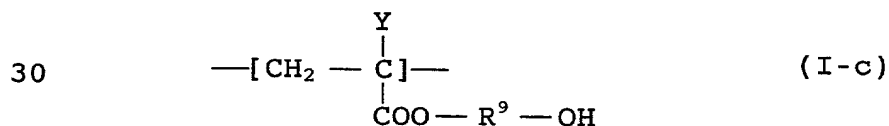
(2) the coating layer (II) is a thermally cured layer of a resin composition containing 15 to 35 % by weight of the component a, 55 to 75 % by weight, as R²SiO_{3/2}, of the component b and 3 to 20 % by weight, as SiO₂, of the component c.

12. The transparent plastic composite material of claim 1, wherein:

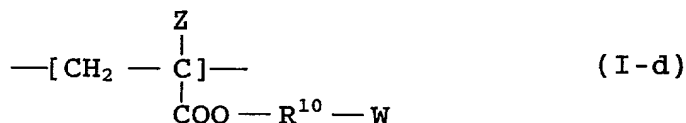
(1) the coating layer (I) is formed of a resin composition containing 100 parts by weight of an acrylic copolymer resin which is formed of recurring units of the following formulae (I-a), (I-c) and (I-d),



wherein R¹ is as defined in the foregoing formula (I-a),

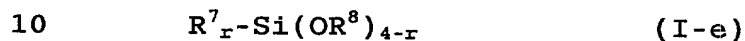


wherein Y and R⁹ are as defined in the foregoing formula (I-c),



wherein Z, R¹⁰ and W are as defined in the foregoing
5 formula (I-d),

and which has a (I-a):(I-c):(I-d) unit ratio in the
range of from 94.7-50:5-40:0.3-15, a mixture (as R⁷_rSiO_{4-x/2})
of hydrolysis condensates of a compound of the
formula (I-e),



wherein R⁷, R⁸ and r are as defined in the foregoing
formula (I-e), the mixture having such an amount that
the ratio of the acrylic copolymer resin:the hydrolysis
condensates comes to be 99:1 to 60:40 by weight, a
15 melamine resin in such an amount that the amount thereof
per 100 parts by weight of the total of the acrylic
copolymer resin and the hydrolysis condensates comes to
be 3 to 15 parts by weight, and 3 to 60 parts by weight,
per 100 parts by weight of the acrylic copolymer resin,
20 of an ultraviolet absorbent, the ultraviolet absorbent
having a solubility of 1.5 g/L or less in a solvent
mixture containing 100 parts by weight of isopropanol,
30 parts by weight of methanol and 15 parts by weight of
water when measured at 25°C, and

25 (2) the coating layer (II) is a thermally cured
layer of a resin composition containing 15 to 35 % by
weight of the component a, 55 to 75 % by weight, as
R²SiO_{3/2}, of the component b and 3 to 20 % by weight, as
SiO₂, of the component c.

30

13. The transparent plastic composite material of claim
1, wherein the transparent plastic substrate is made of
an aromatic polycarbonate resin.

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14. The transparent plastic composite material of claim 1, which has a thickness in the range of from 0.001 to 10 mm.

5 15. The transparent plastic composite material of claim 1, wherein, when subjected to a 1,000-rotation Taber abrasion test (ASTM D1044) using a CS-10F abrasion wheel supplied by Calibrase under a load of 500 g, the transparent plastic composite material shows a change of
10 2 % or less between its haze values before and after the test.

16. The transparent plastic composite material of claim 1, which substantially does not show any occurrence of
15 cracking on the surface thereof after maintained in boiling water for 3 hours.

17. An organic window glass made of the transparent plastic composite material recited in claim 1.

20

18. An organic window glass for a car or an aircraft, which is made of the transparent plastic composite material recited in claim 1.

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ABSTRACT

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A surface-protected plastic composite material comprising a transparent plastic, a coating layer (I) as
5 a first layer stacked on the transparent plastic and a thermally cured coating layer (II) as a second layer stacked on the first layer, the coating layer (I) being formed of a resin composition containing at least 50 % by weight, based on the resin content thereof, of an
10 acrylic resin which is an acrylic resin containing at least 50 mol% of recurring unit based on an alkyl methacrylate, the thermally cured coating layer (II) being made of an organosiloxane resin formed from the following components a, b and c,
15 (A) colloidal silica (component a),
(B) a hydrolysis condensate (component b) of a trialkoxysilane,
(C) a hydrolysis condensate (component c) of a tetraalkoxysilane,
20 the organosiloxane resin containing 5 to 45 % by weight of the component a, 50 to 80 % by weight of the component b and 2 to 30 % by weight of the component c, and use of the composite material as a window glass.

The present invention provides a transparent plastic
25 composite material that is remarkably improved in abrasion resistance and anti-peeling properties.

Dkt. No. OHSB-304**DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (*if only one name is listed below*) or an original, first and joint inventor (*if plural names are listed below*) of the subject matter which is claimed and for which a patent is sought on the invention entitledSUFACE-PROTECTED TRANSPARENT PLASTIC COMPOSITE MATERIAL_____, the specification of which:
(check one) ☐ is attached hereto ☒ was filed on January 31, 2000 as International Application Serial No. PCT/JP00/00515 and was amended on _____ (*if applicable*).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States, listed below and have also identified below any foreign application for patent or inventor's certificate, or PCT international application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed
No. <u>11-024079</u>	<u>Japan</u>	<u>01/02/1999</u>	<input checked="" type="checkbox"/> <input type="checkbox"/>
(NUMBER)	(COUNTRY)	(FILED D/M/Y)	YES NO
No. <u>11-129942</u>	<u>Japan</u>	<u>11/05/1999</u>	<input checked="" type="checkbox"/> <input type="checkbox"/>
(NUMBER)	(COUNTRY)	(FILED D/M/Y)	YES NO
_____	_____	_____	<input type="checkbox"/> <input type="checkbox"/>
(NUMBER)	(COUNTRY)	(FILED D/M/Y)	YES NO
_____	_____	_____	<input type="checkbox"/> <input type="checkbox"/>
(NUMBER)	(COUNTRY)	(FILED D/M/Y)	YES NO
_____	_____	_____	<input type="checkbox"/> <input type="checkbox"/>
(NUMBER)	(COUNTRY)	(FILED D/M/Y)	YES NO
_____	_____	_____	<input type="checkbox"/> <input type="checkbox"/>
(NUMBER)	(COUNTRY)	(FILED D/M/Y)	YES NO

I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s), or §365(c) of any PCT international application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

_____ (APPLICATION SERIAL NO.)	_____ (FILING DATE)	_____ (STATUS)
_____ (APPLICATION SERIAL NO.)	_____ (FILING DATE)	_____ (STATUS)

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or document or any patent issuing thereon.

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